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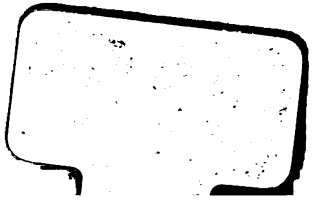
CHEMISTRY
INORGANIC & ORGANIC

DRINKWATER



SYNOPSIS OF CHEMISTRY,

INORGANIC AND ORGANIC.

TO ASSIST STUDENTS PREPARING FOR EXAMINATIONS.

BY

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PREFACE.

In these days of superabundance of Chemical Literature, some apology is needed for introducing yet another Chemical volume to public notice.

Although now published as a whole for the first time, several portions of this book have been for a considerable period in circulation amongst the members of my Classes, and have proved of great assistance in preparing for examination my Students, many of whom have not the time to collect and arrange scattered facts as presented in the Text-Books.

This work has been drawn up with special regard to the Edinburgh Examinations, and this explains the apparent incompleteness of that portion relating to Organic Chemistry. To have given a complete synopsis of this branch would have swelled the book very much beyond its present size. I have, therefore, only considered those Organic Compounds which are mentioned in the Edinburgh University Regulations.

It is not intended to be used as a Text-Book, but rather as a companion to a larger and fuller treatise, and will, I hope, take the place of the Note-Book in recalling the principal facts of the Science in the unsettled and troubled times which precede examination.

To save space I have used the sign θ to signify the application of heat, and the mark $\sqrt{\quad}$ placed over a compound to indicate a precipitate.

I must express my thanks to my colleague Dr. LITTLEJOHN for his valuable aid in revising the proof-sheets.

T. W. D.

CHEMICAL LABORATORY,
EDINBURGH SCHOOL OF MEDICINE,
September 1882.

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TABLE OF SYMBOLS AND ATOMIC WEIGHTS.

Names.	*Symbols.*	*Combining Weights.*
Aluminium	Al	27·4
Antimony	Sb	122
Arsenic	As	75
Barium	Ba	137
Beryllium	Be	9·3
Bismuth	Bi	210
Boron	B	11
Bromine	Br	80
Cadmium	Cd	112
Caesium	Cs	133
Calcium	Ca	40
Carbon	C	12
Cerium	Ce	92
Chlorine	Cl	35·5
Chromium	Cr	52·2
Cobalt	Co	58·7
Copper	Cu	63·5
Didymium	D	95
Erbium	E	112·6
Fluorine	F	19
Gold	Au	197
Hydrogen	H	1
Indium	In	113
Iodine	I	127
Iridium	Ir	198
Iron	Fe	56
Lanthanum	La	92
Lead	Pb	207
Lithium	Li	7

TABLE OF SYMBOLS AND ATOMIC WEIGHTS—*continued.*

Names.	*Symbols.*	*Combining Weights.*
Magnesium	Mg	24
Manganese	Mn	55
Mercury	Hg	200
Molybdenum	Mo	96
Nickel	Ni	58·7
Niobium	Nb	94
Nitrogen	N	14
Osmium	Os	199·2
Oxygen	O	16
Palladium	Pd	106·6
Phosphorus	P	31
Platinum	Pt	197·5
Potassium	K	39·1
Rhodium	Rh	104·4
Rubidium	Rb	85·4
Ruthenium	Ru	104·4
Selenium	Se	79·5
Silver	Ag	108
Silicon	Si	28
Sodium	Na	23
Strontium	Sr	87·5
Sulphur	S	32
Tantalum	Ta	182
Tellurium	Te	129
Thallium	Tl	204
Thorium	Th	231·5
Tin	Sn	118
Titanium	Ti	50
Tungsten	W	184
Uranium	U	120
Vanadium	V	51·3
Yttrium	Y	61·6
Zinc	Zn	65·2
Zirconium	Zr	89·6

ERRATA.

Page 3, Acid radical monads, lines 4, 5, and 6, *for* Bi, BiO_3, and BiO, *read* Br, BrO_3, and BrO.

Page 6, line 15 from bottom, *for* 3·2 *read* 32.

Page 91, line 10 from bottom, *for* Hg_2Cl_2 *read* $HgCl_2$.

SYNOPSIS

OF

CHEMISTRY.

DEFINITIONS.

CHEMISTRY.—Science which treats of matter in a state of change.

Three forms of matter :—

(*a.*) Solid—if cohesive force in ascendancy.
(*b.*) Gas—if repulsive „ „
(*c.*) Liquid—if repulsive and cohesive powers are balanced. Matter on this earth is usually mixed.

ANALYSIS is the separation of mixed matter into elementary matter.

SYNTHESIS is the putting together of elementary matter to form compounds.

ELEMENTS.—The simplest form of matter. They are sixty-five in number, and are divided into two groups, *non-metallic* and *metallic*. There are thirteen non-metallic elements.

SYMBOL.—A sign representing an element, and a certain quantity of that element. The sign consists of a letter or letters contained in the Latin name.

MOLECULE.—The smallest portion of an element which can exist in the free condition.

ATOM.—The smallest portion of an element which can exist in the combined state.

CHEMICAL AFFINITY.—The force which produces chemical action subject to certain laws.

LAWS OF COMBINATION.

1*st.* LAW OF QUANTITIES.—A definite chemical compound always contains the same elements in the same fixed proportion.

Example.—FeS (*Ferrous Sulphide*) always contains iron and sulphur, but nothing else, and always in the proportion of 56 parts of iron to 32 parts of sulphur.

2*d.* LAW OF MULTIPLES.—When two elements unite in more than one proportion, the resulting compound contains a fixed quantity of one element, and a varying quantity of the other; the varying quantities being in some simple multiple of the first compound.

Example.—Nitrogen and oxygen form five oxides—

N_2O = 28 to 16
N_2O_2 = 28 to 32
N_2O_3 = 28 to 48
N_2O_4 = 28 to 64
N_2O_5 = 28 to 80

3*d.* LAW OF RECIPROCAL PROPORTIONS.—The proportion in which any two elements unite with a third are the proportions in which they unite with one another.

Example.—H and I unite in proportion of 1 to 127
H and Cl ,, ,, 1 to 35·5
Therefore Cl and I ,, ,, 35·5 to 127

SALT-RADICAL.—A *compound* which unites with H to form an ACID, and a metal to form a SALT.

HALOGEN.—An *element* which has the same properties as a salt-radical.

TABLE OF ATOMICITY.

BASIC RADICALS.

Monads.	Dyads.	Triads.	Tetrads.	Pentads.	Hexads.
H	Ca	Au	Sn		Fe_2^{iv}
K	Ba	Bi	Pt		Al_2
Na	Sr	Sb			Cr_2^{iv}
Ag	Zn	C_3H_5			
NH_4	Mg				
CH_3	Cd				
C_2H_5	Pb				
	Cu				
	Cu_2				
	Hg				
	Hg_2				
	Sn, Fe, Co, Ni } ous.				

ACID RADICALS.

Monads.	Dyads.	Triads.	Tetrads.
Cl	O	PO_4	$FeCy_6^{iv}$
ClO	CO_3	AsO_4	SiO_4
ClO_3	S	AsO_3	As_2O_7
Bi	SO_2	$FeCy_6^{iii}$	P_2O_7
BiO_3	SO_4	$C_6H_5O_7$	
BiO	S_2O_3		
I	C_2O_4		
IO_3	$C_4H_4O_6$		
NO_2	$C_3H_5O_3$		
NO_3			
Cy			
PH_2O_2			
PO_3			
CNO			
$C_2H_3O_2$			
CNS			
CHO_2			

Use of the Table.

A salt consists essentially of a basic radical and an acid radical. These two radicals must balance each other in the matter of atomicity or quantivalence. If, therefore, we know the respective atomicity of both basic and acid radicals, it is an easy matter to unite the formula of a salt; for we must make the two parts equal each other, so to speak, by means of figures if they do not do so naturally. A few examples will make this clearer.

What is the formula of nitrate of potash? We look first amongst the basic radicals for potassium, and we find K amongst the monads; then amongst the acid radicals for nitric acid radical, NO_3, and we find that is also amongst the monads; therefore $K'NO'_3$ is the formula, for a monad unites with a monad. But supposing the formula of calcic nitrate is required, we find Ca amongst the dyads, and NO_3, as before, a monad. Now a dyad will not unite with one monad, it requires two; therefore calcic nitrate is $Ca''2NO'_3$

Again, required the formulæ of oxalate of lime and oxalate of soda.

Ca = Dyad, and C_2O_4 = Dyad; therefore the formula is $Ca''C_2O''_4$

Na = Monad, and C_2O_4 = Dyad; therefore the formula is Na_2' $C_2O''_4$; two monads being required to balance one dyad.

Again, required the formula of ferric sulphate. Fe_2 by the table is a hexad, or has a value equal to six monads. The sulphuric acid radical is a dyad, or has a value equal to two monads; therefore the formula is $Fe_2^{vi}3SO''_4$

CHEMICAL SUMS.

Correction of Volume.

(*a.*) *For Temperature.*—Gases expand by heat $\frac{1}{273}$ of their volume for each degree Centigrade, and contract by cold in the same ratio, therefore at a temperature of 273° below zero there is theoretically no heat and no volume. According to Charles Law, "The volume of any gas varies directly as the absolute temperature;" the following formula will therefore give us the needed correction for any temperature:—

$$\text{As } 273 + \begin{matrix}\text{Temp. at}\\ \text{measurement}\end{matrix} : 273 + \begin{matrix}\text{Temp.}\\ \text{required}\end{matrix} :: \begin{matrix}\text{Observed}\\ \text{volume}\end{matrix} : x$$

$$\text{Or, As } 273 + t^m : 273 + t^r :: OV. : x$$

Example.—100 cubic centimetres of oxygen are measured @ 15° C., what will they measure @ 0° C.?

$$\text{As } 273 + t^m : 273 + t^r :: OV : x$$

$$\begin{matrix}273 & 273\\ 15 & 0\\ \hline 288 & 273\end{matrix} :: 100 : x$$

$$\frac{273 \times 100}{288} = 94{\cdot}79 \text{ c. c. @ } 0° \text{ C.}$$

Answer.

(*b.*) Correction for Pressure.—Boyle's law states that the volume of any gas varies *inversely* as the pressure to which it is subjected. The following formula will give the correction for pressure:—

$$\text{As } \begin{matrix}\text{The required}\\ \text{pressure}\end{matrix} . \begin{matrix}\text{The observed}\\ \text{pressure}\end{matrix} . \begin{matrix}\text{The observed}\\ \text{volume}\end{matrix} : x$$

$$\text{Or, As R.P. : O.P. : : O.V. : } x$$

Example.—100 c. c. of hydrogen are measured @ 752 millimetres, what will they measure @ 760 millimetres (m.m.)?

$$\text{As RP : OP :: OV} : x$$

$$760 : 752 :: 100 : x$$

$$\frac{752 \times 100}{760} = 98{\cdot}95 \text{ c. c. @ } 760.$$

Answer.

Converting Volume of Gas to Weight of Gas.

11·2 litres of any elementary gas weighs its atomic weight in grammes, and half its molecular weight if a compound gas.

For example, 11·2 litres of O weigh 16 grammes
" N " 14 "
" Cl " 35·5 "
Or 11·2 litres of HCl " 18·25 "
" CH_4 " 8 "
" SO_2 " 32 "

} At normal T° and P.

If, therefore, we wish to know the weight of 5 litres of oxygen gas—

$$\text{As } 11{\cdot}2 : 16 :: 5 : x$$

$$\frac{16 \times 5}{11{\cdot}2} = 7{\cdot}14 \text{ grammes.}$$

Conversely, if the weight is given to convert to volume, the following example will show the method of calculation.

What is the volume of 32 grammes of oxygen?

$$\text{As } 16 : 11{\cdot}2 :: 32 : x$$

$$\frac{11{\cdot}2 \times 3{\cdot}2}{16} = 22{\cdot}4 \text{ litres.}$$

Example of Sums based on Equations.

In 100 grammes of sulphuric acid (H_2SO_4), how much hydrogen @ normal T and P? How much zinc required to displace it, and how much sulphate of zinc will be produced? H = 1. Zn = 65·2. S = 32. O = 16.

$$H_2SO_4 + Zn = ZnSO_4 + H_2$$
$$98 + 65{\cdot}2 = 161{\cdot}2 + 2$$

(The figures below the symbols are the atomic and molecular weights.)

(*a.*) Quantity of H.

$$\text{As } 98 : 2 :: 100 : x$$

$$\frac{2 \times 100}{98} = 2{\cdot}04 \text{ grammes.}$$

(*b.*) Volume of H.

Gram. Lrs. Gram.
As 1 : 11·2 : : 2·04 : x

$$\frac{11{\cdot}2 \times 2{\cdot}04}{1} = 22{\cdot}84 \text{ litres.}$$ Answer I.

(*c.*) Quantity of Zinc.

According to equation, 2 grammes H require 65·2 of Zn.

As 2 : 65·2 : : 2·04 : x

$$\frac{65{\cdot}2 \times 2{\cdot}04}{2} = 66{\cdot}5 \text{ grammes of Zn.}$$

Answer II.

(*d.*) Quantity of $ZnSO_4$

According to equation 65·2 grammes of Zn produce 161·2 grammes of $ZnSO_4$

As 65·2 : 161·2 : : 66·5 : x

$$\frac{161{\cdot}2 \times 66{\cdot}5}{65{\cdot}2} = 164{\cdot}48.$$

Quantity of $ZnSO_4$

Answer III.

VARIOUS CLASSES OF SALTS.

1*st.* Normal Salts.—Where the whole of the hydrogen is displaced by an equivalent quantity of a metal, or basic radical.

Acid.	Salt.
$\left.\begin{matrix}H\\H\end{matrix}\right\}SO_4$	$\left.\begin{matrix}Na\\Na\end{matrix}\right\}SO_4$

2*d.* Acid Salts.—Where only part of the hydrogen is displaced.

Acid.	Salt.
$\left.\begin{matrix}H\\H\end{matrix}\right\}SO_4$	$\left.\begin{matrix}Na\\H\end{matrix}\right\}SO_4$

3d. BASIC SALTS.—Where part of acid radical is replaced by oxygen.

Acid.	Normal Salt.	Basic Salt.
HNO_3	$Bi''' 3NO'_3$	$BiONO_3$
	$Bi\begin{cases} NO_3 \\ NO_3 \\ NO_3 \end{cases}$	$Bi'''\begin{cases} O'' \\ NO_3 \end{cases}$

NOMENCLATURE OF SALTS.

Acids ending in OUS form salts in ITE.

Example.—Sulphurous acid forms sulphites.

Acids ending in IC form salts in ATE.

Example.—Sulphuric acid forms sulphates.

Elements form salts ending in IDE.

Example.—Iron and sulphur form iron sulphide.

NON-METALLIC ELEMENTS.

Oxygen.—O = 16, Dyad.

Occurrence.—Free in air, combined in water and metallic oxides.

Properties.—Colourless, tasteless, inodorous gas, slightly soluble in H_2O. Under ordinary circumstances a supporter of combustion. Combines with all the elements but one, Fl.

Preparation.—1*st.* From certain oxides.

TABLE I.

The Oxides which give off O *on application of Heat.*

Oxides,	BaO_2	MnO_2	CrO_3	Au_2O_3	PtO_2	Ag_2O	HgO	Pb_3O_4
Residues,	BaO.	Mn_3O_4.	Cr_2O_3.	Au.	Pt.	Ag	Hg	PbO

2*d*. From certain salts.

θ. $KClO_3 = KCl + O_3$ and $ZnSO_4 = ZnO + SO_2 + O$

3*d*. Electrolysis of H_2O.

O is evolved at the positive pole.

Three groups of Oxides.

(*a*.) Basic, forming salts with acids, FeO
(*b*.) Acid, „ „ metals, CrO_3
(*c*.) Neutral, not forming combinations, MnO_2

Ozone.—Allotropic oxygen. (O_2O)
Occurrence.—Free in air.
Properties.—Colourless gas with powerful odour; oxidizer and bleacher.
Preparation.—By electric discharge in air or oxygen.
Test.—Sets free iodine from KI.

$$(O_2O) + 2KI + H_2O = 2KHO + O_2 + I_2$$

Hydrogen = 1, Monad.

Occurrence.—Not free in nature. Combined in H_2O, and all animal and vegetable substances.
Properties.—Colourless, odourless gas, lightest of all known bodies. Inflammable. Reducing agent.
Preparation.—From water by—
(*a*.) Electrolysis.
(*b*.) By certain metals.

TABLE II.

* *Metals which decompose Water @ ordinary temperature.*					
K	produces	KHO	Ca	produces	Ca2HO
Na	„	NaHO	Ba	„	Ba2HO
			Sr	„	Sr2HO

* These metals are also oxidized by dry air.

(*c.*) By acting on acids with metals.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

(*d.*) By acting on certain hydrates with metals.

$$\theta.\ Zn + 2KOH = ZnK_2O_2 + H_2$$

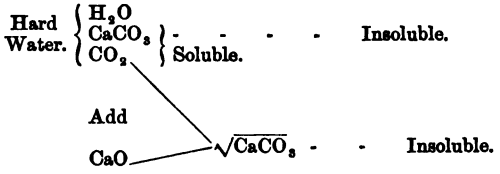
WATER.

Prepared by synthesis of its elements. Occurs in nature as spring water, &c., in an impure condition from the solution of certain salts.

Hard water due to presence of $CaCO_3$ and $CaSO_4$ principally. The $CaCO_3$ is dissolved by free CO_2; the $CaSO_4$ by pressure; $CaCO_3$ precipitated by boiling, hence hardness due to it called removeable hardness; $CaSO_4$ not so removeable, hence confers the property of permanent hardness.

Clarke's process for softening water by adding lime (CaO) removes free CO_2

Diagram representing Clarke's process.



Water unites with acid oxides to form acids:

$$e.g.,\ H_2O + SO_3 = H_2SO_4$$

It also unites with basic oxides to form hydrates:

$$e.g.,\ K_2O + H_2O = 2KHO$$

TABLE III.

Action of Heat on Hydrates.

KHO, NaHO } = no action.

$Ca2HO = CaO + H_2O$

$Ba2HO = BaO + H_2O$

Hydrates of all the heavy metals are decomposed into water and oxide.

Water of Crystallisation.—Water on which the shape and colour of the crystal depend. It can be driven off at 100° C.

Water of Constitution.—Water on which the chemical constitution of the salt depends.

θ. 100° C. $CuSO_45H_2O = CuSO_4H_2O + 4H_2O$
Water of crystallisation.

θ. 199° C. $CuSO_4H_2O = CuSO_4 + H_2O$
Water of constitution.

Peroxide of Hydrogen, H_2O_2.

Properties.—Colourless liquid, pungent taste. Bleacher. Acts as an oxidizing and reducing agent. Decomposed by heat. θ. $H_2O_2 = H_2O + O$

Prep.—$BaO_2 + CO_2 + H_2O = \overline{BaCO_3} + H_2O_2$

Nitrogen.—N = 14, Triad and Pentad.

Occurrence.—Free in air, combined in animal and vegetable substances.

Properties.—Colourless gas with negative properties.

Preparation.—(*a.*) By abstracting O from air by means of P or Cu, &c.

(*b.*) By abstracting the hydrogen from ammonia (NH_3) by chlorine.

$3Cl + 2NH_3 = 6HCl + N_2$

(*c.*) By heating certain salts.

θ. $NH_4NO_2 = N_2 + 2H_2O$
Ammonic nitrite.

OXIDES OF NITROGEN.

TABLE IV.

Preparation of all the Oxides of Nitrogen from a Nitrate or Nitric Acid.

$$2AgNO_3 + Cl_2 = 2AgCl + O + N_2O_5$$
$$4HNO_3 + Sn = SnO_2 + 2H_2O + 2N_2O_4$$
$$2HNO_3 + As_2O_3 = As_2O_5 + H_2O + N_2O_3$$
$$8HNO_3 + 3Cu = 3Cu2NO_3 + 4H_2O + N_2O_2$$
$$10HNO_3 + 4Zn = 4Zn2NO_3 + 5H_2O + N_2O$$
$$2KNO_3 + 5Zn = 5ZnO + K_2O + N_2$$
$$2KNO_3 + 6KHO + 8Zn = 8ZnO + 4K_2O + 2NH_3$$

NITRIC ANHYDRIDE, N_2O_5.

White deliquescent solid.

Preparation.—See Table IV. Forms with water nitric acid.

Nitric acid.—HNO_3

Preparation—θ $\begin{cases} NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3 \\ NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3 \end{cases}$

HNO_3 acts in three ways:

(*a.*) As an acid.

(*b.*) As an oxidizing agent.

(*c.*) As a producer of nitro-substitution compounds.

TABLE V.

Action of Nitric Acid on Metals, &c.

Strong.	*Dilute.*
Au Pt Al Fe. = No action.	Au Pt Al + No action.
$Zn = Zn2NO_3 + N_2O + H_2O$	$Fe = Fe_2 6NO_3 + NO$
	$Zn = Zn2NO_3 + NH_4NO_3 + H_2O$
$Sn = SnO_2 + N_2O_4 + H_2O$	No action unless boiled for some time.
$Sb = Sb_2O_5 + N_2O_3 + NO$	No action.
$As = As_2O_5 + N_2O_3 + NO$	$As_2O_3 + NO$
Pb, Bi, Cu, Ag = Nitrates + NO	The same.

TABLE V.—*continued.*

On Acids and Acid Radicals.

Oxalic = NO + CO_2 + H_2O
Sulphurous = NO + H_2SO_4
Hydrochloric = $NOCl_2$ + Cl
Thio-sulphuric = NO + S + H_2SO_3 + H_2SO_4
S = H_2SO_4
P = H_3PO_4
I = HIO_3

On Hydrocarbons.

Produces nitro-substitution compounds:

e.g., $C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$

TABLE VI.

Reactions of Nitrates.

All are soluble.
When heated with H_2SO_4 = HNO_3 and sulphates.
,, ,, H_2SO_4 + $FeSO_4$ = NO and sulphates.

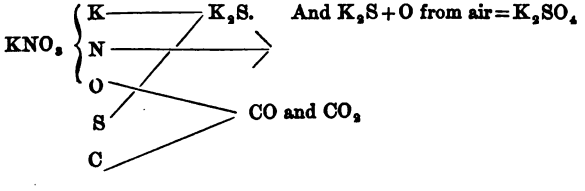
Action of Heat.

All are decomposed.
$KNO_3 = KNO_2 + O$
$NaNO_3 = NaNO_2 + O$
$NH_4NO_3 = N_2O + 2H_2O$

The nitrates of the heavy metals give off oxygen, nitric peroxide, and leave an oxide:

e.g., $Cu2NO_3 = CuO + N_2O_4 + O$

Diagram explaining Explosion of Gunpowder.



Nitric Peroxide, N_2O_4.

Reddish brown gas, condensible to a brown liquid.

Preparation.—(*a.*) By decomposing nitrate by heat.

$$\theta.\ Cu2NO_3 = CuO + O + N_2O_4$$

(*b.*) $N_2O_2 + O_2 = N_2O_4$

Reactions.—$N_2O_4 + H_2O = HNO_3 + HNO_2$

$N_2O_4 + 2KHO = KNO_3 + KNO_2 + H_2O$

Nitrous Anhydride, N_2O_3.

Reddish brown gas, condensible to a blue liquid.

Preparation.—(See Table IV.) Forms with water HNO_2 nitrous acid, which is unstable.

$$3HNO_2 = HNO_3 + N_2O_2 + H_2O$$

Nitrites formed by absorption of N_2O_3 by hydrates.

$$2KHO + N_2O_3 = 2KNO_2 + H_2O$$

Ammonium nitrite an exception.

$$N_2O_3 + 2NH_3 = 2N_2 + 3H_2O$$

This explains the following:—

$$\theta.\ 2NH_4Cl + 2KNO_2 = 2KCl + N_4 + 4H_2O$$

Preparation of ammonium nitrite.

$$\theta.\ Pb2NO_3 + Pb_2 = Pb2NO_2 + 2PbO$$

$$Pb2NO_2 + (NH_4)_2SO_4 = \sqrt{PbSO_4} + 2NH_4NO_2$$

Action of Heat on Nitrites.

All decomposed leave an oxide and give off N_2O_3.

$$2KNO_2 = K_2O + N_2O_3$$

Nitric Oxide, N_2O_2.

Colourless gas, supports combustion of P or C.

Preparation.—(See Table IV.).

θ. $2KNO_3 + 6FeSO_4 + 4H_2SO_4 = K_2SO_4 + 3Fe_23SO_4 + 4H_2O + N_2O_2$

Nitrous Oxide, N_2O.

(Laughing Gas).—Colourless gas, sweet taste, soluble in H_2O. Supports combustion like oxygen, but volume of gas unchanged.

Preparation.—(See Table IV.)

Ammonia, NH_3.

Colourless gas, very soluble in H_2O, pungent odour. Combines directly with acids to form salts. Inflammable with difficulty in air, with ease in oxygen. Undergoes slow oxidation to form NH_4NO_2 and NH_4NO_3.

Preparation.—

(*a.*) By heating ammoniacal salts with any alkaline hydrate.

θ. $2NH_4Cl + Ca2HO = 2NH_3 + CaCl_2 + 2H_2O$

(*b.*) From a nitrate. (See Table IV., page 12.)

It unites with anhydrous acids to form a distinct and peculiar set of salts.

$$2NH_3 + CO_2 = \underbrace{NH_4NH_2CO_2}_{\text{Carbamate of ammonia.}}$$

Chloride of Nitrogen, NCl_3.—Oily liquid, very unstable and explosive.

Preparation.—$NH_4Cl + 3Cl_2 = 4HCl + NCl_3$.

IODIDE OF NITROGEN (NHI_2?).—Black powder, unstable and explosive.

Preparation.—$NH_3 + 2I_2 = 2HI + NHI_2$

Carbon = 12, Tetrad.

Occurrence.—Free and combined in nature.

Properties.—Allotropic. Three principal varieties—

(*a.*) Diamond; (*b.*) Graphitoidal; (*c*) Amorphous.

(*a.*) and (*b.*) found native.

Preparation of (*c.*) two varieties, animal and vegetable.

By distillation of wood = Wood charcoal.
" " coal = Coke.
" " bones = Animal charcoal.

TABLE VII.

Products of Distillation of Wood.

Solids.—Charcoal.

Liquids.—Watery Liquor.
Tar.

Gases.—CH_4, CO, CO_2, H, &c.

Watery Liquor. Neutralised with Ca2HO and distilled = CH_3HO. H_2SO_4 added to the residue and again distilled = $HC_2H_3O_2$.

Tar. Agitated with NaHO to dissolve creosote, which is precipitated with HCl.

OXIDES OF CARBON.—(*a.*) CARBONIC ACID, CO_2

Occurrence.—Free to a limited extent in air, largely combined as carbonates.

Properties.—Colourless, heavy gas, neither inflammable nor supporter of combustion, very soluble in water, condensible to a liquid and solid. Unites

with metallic oxides to form carbonates. Decomposed by fused K.

$$\theta.\ 3CO_2 + 2K_2 = 2K_2CO_3 + C$$

Preparation.—(*a.*) See Table VIII.

(*b.*) $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$

TABLE VIII.

Action of Heat on Carbonates.

* Carbonates of Alkalies. { K_2CO_3, Na_2CO_3 } no action. * { $KHCO_3 = K_2CO_3 + CO_2 + H_2O$; $NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$ }

$(NH_4)_2CO_3$ sublimes unchanged.

All other carbonates leave an oxide, and give off CO_2

$\theta.\ CaCO_3 = CaO + CO_2$

* These are the only soluble carbonates. The carbonates of heavy metals are soluble in water, containing excess of CO_2

Carbonic Oxide, CO.

Properties.—Colourless gas, poisonous; reducing agent; inflammable, burning to CO_2

Preparation.—($\theta.$) $CO_2 + C = 2CO$

($\theta.$) $H_2C_2O_4 + H_2SO_4 = H_2SO_4,H_2O + CO + CO_2$

Action of sulphuric acid, strong and dilute, on K_4FeCy_6

(*Strong*) $\theta.\ K_4FeCy_6 + 6H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(*Dilute*) $\theta.\ 2K_4FeCy_6 + 6H_2SO_4 + x\ H_2O = 6KHSO_4 + K_2Fe(FeCy_6) + x\ H_2O + 6HCy$

Reactions.—Has no action on aqueous alkaline hydrates, but if fused.

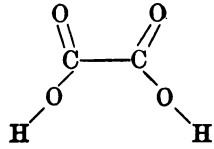
$$\theta.\ KHO + CO = KCHO_2$$

$$CO + Cl_2 = COCl_2 \text{ (phosgene gas).}$$

SESQUIOXIDE OF CARBON, C_2O_3.—Not yet isolated; exists in hydrated condition as $H_2C_2O_4$ (oxalic acid).

RELATION OF OXALIC ACID TO CYANOGEN.

$N{\equiv}C{-}C{\equiv}N$



HOO replaces N, hence $(CN)_2$ is the nitryl of oxalic acid.

Preparation of an oxalate from cyanogen :

$$\theta.\ 2CN + 2KHO + 2H_2O = K_2C_2O_4 + 2NH_3$$

Usual preparation.—Sawdust moistened with aqueous KHO and heated, the cellulose is oxidized to oxalic acid :

$$C_6H_{10}O_5 + O_9 = 3H_2C_2O_4 + 2H_2O$$

which unites with K to form $K_2C_2O_4$. Dissolve in water and treat with Ca2HO :

$$K_2C_2O_4 + Ca2HO = \sqrt{CaC_2O_4} + 2KHO,$$

finally $CaC_2O_4 + H_2SO_4 = \sqrt{CaSO_4} + H_2C_2O_4$

Reactions of Aqueous Solution.

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$$

$$3H_2C_2O_4 + 2AuCl_3 = 6HCl + 6CO_2 + \sqrt{Au_2}$$

$$5H_2C_2O_4 + 2HIO_3 = 10CO_2 + 6H_2O + I_2$$

TABLE IX.

Action of Heat in Oxalic Acid and Oxalates.

$\theta.$ $\left\{\begin{array}{l} H_2C_2O_4 = CO_2 + HCHO_2 \\ HCHO_2 = CO + H_2O \end{array}\right.$

$$Ag_2C_2O_4 = \sqrt{Ag_2} + 2CO_2$$

$$2(PbC_2O_4) = Pb_2O + 3CO_2 + CO$$

All other oxalates give off CO and leave a carbonate.

The only soluble oxalates are those of the alkalies.

Hydrocarbons.

General characters.—Colourless inflammable substances, consisting entirely of hydrogen and carbon. They are inflammable, and burn to CO_2 and H_2O with full supply of air. They are usually considered with the Organic Chemistry; it is convenient, however, to study three of them at this stage.

Marsh Gas, CH_4 or CH_3H.—Hydride of methyl, methane, fire-damp, light carburetted hydrogen.

Occurrence.—Free in nature in marshes, also in blowers in coal seams.

Preparation.—$\theta.$ $KC_2H_3O_2 + KHO = K_2CO_3 + CH_4$

$\theta.$ $CS_2 + 2H_2S + 4Cu = 4CuS + CH_4$

Properties.—Colourless inflammable gas, lighter than air.

TABLE X.

Action of Chlorine in Marsh Gas.

$$CH_4 + Cl_2 = CH_3Cl + HCl$$
$$CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl$$
$$CH_4 + 3Cl_2 = CHCl_3 + 3HCl$$
$$CH_4 + 4Cl_2 = CCl_4 + 4HCl$$

Forms an explosive mixture when mixed with air in oxygen in sufficient quantity.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
2vol. + 4vol. = 2vol. + 4vol.

Olefiant Gas, C_2H_4.

Heavy carburetted hydrogen or ethylene.

Occurrence.—In coal gas.

Preparation.—

TABLE XI.

Action of Sulphuric Acid on Alcohol.

(*a.*) Acid in excess and high T°.

θ. $C_2H_5HO + H_2SO_4 = H_2SO_4H_2O + C_2H_4$, olefiant gas.

(*b.* Alcohol in excess and low T°.

θ. $C_2H_5HO + H_2SO_4 = C_2H_5HSO_4 + H_2O$

$C_2H_5HSO_4 + C_2H_5HO = H_2SO_4 + (C_2H_5)_2O$, ether.

Reactions.—$C_2H_4 + Cl_2 = C_2H_4Cl_2$ (Dutch liquid).

If $\frac{1}{3}$ C_2H_4 and $\frac{2}{3}$ Cl are mixed and ignited—

$$C_2H_4 + 2Cl_2 = 4HCl + \sqrt{C_2}$$

If passed into $H_2SO_4 = \underset{\text{Sulphovinic acid.}}{C_2H_5HSO_4}$

This reaction used in the synthesis of alcohol.

Acetylene, C_2H_2.

Colourless gas with distinctive odour.

Preparation.—By synthesis.

Reactions.—

$$2C_2H_2 + \underset{\substack{\text{Ammoniacal}\\\text{solution.}}}{2Cu_2Cl_2} = \sqrt{Cu_4C_4H_2O} + 4HCl.$$

If passed through $KMnO_4$

$$C_2H_2 + 2O_2 = H_2C_2O_4 \text{ (oxalic acid).}$$

Coal Gas.

TABLE XII.

Products of Distillation of Coal.

Solids.	Coke.	
Liquids.	Watery Liquor. Tar.	Watery Liquor. Neutralised with H_2SO_4 and evaporated = $(NH_4)_2SO_4$ Tar. Distilled for Benzol, C_6H_6 Carbolic acid, C_6H_5HO. Anthracene, $C_{14}H_{10}$
Gases.	$H.CH_4C_2H_4$ CO_2CO, &c.	

STRUCTURE OF FLAME.

Ordinary flame consists of three zones, arranged from within outwards as follows:—

(*a.*) Zone of unburnt gases—non-luminous.
(*b.*) Zone of incomplete combustion—luminous.
(*c.*) Zone of complete combustion—non-luminous.

BLOW-PIPE FLAME.—Consists of two zones only, the external or oxidizing flame, the internal or reducing flame.

The Halogens.—Cl, Br, I, Fl.

They are all monads.

Chlorine.—Cl, 35·5.

Occurrence.—Combined as chlorides.

Properties.—Greenish yellow gas, suffocating odour, very soluble in water, condensible to liquid. Supports combustion of certain metals, phosphorous, and of substances containing hydrogen.

Preparation.—

$$\theta.\ MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

$$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2$$

$$\theta.\ 2HCl + O = H_2O + Cl_2$$

$$\theta.\ \begin{cases} PtCl_4 = Pt + 2Cl_2 \\ AuCl_3 = Au + Cl_3 \end{cases}$$

Electrolysis of HCl.

Reactions.—

TABLE XIII.

Action of Chlorine on Metals.

As = $AsCl_3$	Pb = $PbCl_2$	Ag = AgCl
Sb = $SbCl_5$ (Production of light.)	Fe = Fe_2Cl_6	Cd = $CdCl_2$
Bi = $BiCl_3$ (Production of light.)	Al = Al_2Cl_6	Cu = $CuCl_2$ and Cu_2Cl_2
Sn = $SnCl_4$ (Production of light.)	Zn = $ZnCl_2$	Hg = $HgCl_2$ and Hg_2Cl_2
Au = $AuCl_3$ } below	AuCl } at red	Au } above
Pt = $PtCl_4$ } red heat.	$PtCl_2$ } heat.	Pt } red heat.

On Acids.

$H_2C_2O_4 = HCl + CO_2$	$H_2S_2O_3 = HCl + H_2S_4O_6$
$HNO_2 = HCl + HNO_3$	$H_4FeCy_6 = HCl + H_3FeCy_6$
$H_2S = HCl + S + H_2SO_4$	$HBr = HCl + Br$
$H_2SO_3 = HCl + H_2SO_4$	$HI = HCl + I$

Powerful bleacher and oxidizer. Both properties only exerted in presence of H_2O.

$$Cl_2 + H_2O = 2HCl + O$$

Forms chlorides, all soluble but three:

$$AgCl,\ Hg_2Cl_2,\ Cu_2Cl_2$$

TABLE XIV.

Action of Heat in Chlorides.

$PtCl_4 = Pt + Cl_2$
$AuCl_3 = Au + Cl_3$
$Fe_2Cl_6 = Fe_2O_3 + 3Cl_2$ (in presence of air).

Other chlorides no action. Most of them sublime unchanged.

Hydrochloric Acid, HCl.

Properties.—Colourless gas, very soluble in water.

Preparation.— $\begin{cases} NaCl + H_2SO_4 = NaHSO_4 + HCl \\ NaHSO_4 + NaCl = Na_2SO_4 + HCl \end{cases}$

θ. $2H_2O + 2Cl_2 = 4HCl + O_2$

$H_2 + Cl_2 = 2HCl$

TABLE XV.

Action of HCl *Solution on Metals.*

Strong.	Dilute.
$K = KCl + H$	$KCl + H$
$Na = NaCl + H$	$NaCl + H$
$Mg = MgCl_2 + H$	$MgCl_2 + H$
$Al = Al_2Cl_6 + H$	$Al_2Cl_6 + H$
$Zn = ZnCl_2 + H$	$ZnCl_2 + H$
$Fe = FeCl_2 + H$	$FeCl_2 + H$
Sb = No action	No action.
If heated = $SbCl_3$ and H	
$Sn = SnCl_2 + H$	No action.
$Co = CoCl_2 + H$	$CoCl_2 + H$
$Ni = NiCl_2 + H$	$NiCl_2 + H$
Cu = Slowly covered with crystals of Cu_2Cl_2	No action.

Neither strong or dilute have any action, Hg, Pb, Bi, Ag, Au, Pt.

If *chlorine* be passed into the above solutions—

$FeCl_2 = Fe_2Cl_6$ and $SnCl_2 = SnCl_4$

The others are unaltered.

Action of HCl *on Acids.*

$HNO_3 = NOCl + H_2O + Cl$	$HClO = H_2O + Cl$
$HClO_3 = Cl_2O_4$	$HCrO_3 = CrO_2Cl_2$

Hypochlorous Anhydride, Cl_2O.

Properties.—Greenish yellow gas. Unstable and explosive. Soluble in H_2O to HClO.

Preparation.—θ. $2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O$.

Hypochlorous Acid, HClO.

Preparation.—

$$2HgO + 2Cl_2 + H_2O = \sqrt{Hg_2OCl_2} = 2HClO$$

Reactions.—$HClO + HClO = Cl_2 + H_2O$

$$2HClO + Ag_2O = 2AgCl + H_2O + O_2$$

Forms hypochlorites—

$$HClO + NaHO = NaClO + H_2O$$

TABLE XVI.

Action of Cl *in Alkaline Hydrates.*

(*a.*) Cold.—$2KHO + Cl_2 = KClO + KCl + H_2O$

$2NaHO + Cl_2 = NaClO + NaCl + H_2O$

(*b.*) Hot.—$6KHO + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$

$6NaHO + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$

Bleaching Powder, $CaCl_2,Ca2ClO$

Preparation.—$Ca2HO + 2Cl_2 + CaCl_2Ca2ClO + 2H_2O$

Reactions.—(*a.*) Small quantity of H_2SO_4

$$CaCl_2,Ca2ClO + H_2SO_4 = CaCl_2 + CaSO_4 + 2HClO$$

(*b.*) Excess of H_2SO_4

$$CaCl2Ca2ClO + 2H_2SO_4 = 2CaSO_4 + 2HCl + 2HClO$$

and

$$2HCl + 2HClO = 2Cl_2 + 2H_2O$$

(*c.*) Action of heat. The chloride undergoes no change; the hypochlorite is changed as under:—

$$\theta.\ 3Ca2ClO = 2CaCl_2 + Ca2ClO_3$$

Chlorous Anhydride, Cl_2O_3.

Properties.—Greenish yellow gas.

Preparation. *θ.*
$$\left\{\begin{array}{rl} KClO_3 + HNO_3 &= HClO_3 + KNO_3 \\ H_3AsO_3 + HNO_3 &= H_3AsO_4 + HNO_2 \\ HNO_2 + HClO_3 &= HClO_2 + HNO_3 \\ 2HClO_2 &= Cl_2O_3 + H_2O \end{array}\right\}$$

Reactions.—*θ.* $3Cl_2O_3 + 3H_2O = 2HCl + 4HClO_3$

$Cl_2O_3 + 6HCl = 4Cl_2 + 3H_2O$

Salts unimportant.

Chloric Peroxide, Cl_2O_4.

Properties.—Deep yellow gas.

Preparation.—$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + Cl_2O_4$

Reactions.—$Cl_2O_4 + H_2O = HClO_3 + HClO_2$

$2KHO + Cl_2O_4 = KClO_3 + KClO_2 + H_2O$

Chloric Acid, $HClO_3$.—No known anhydride.

Properties.—Syrupy acid liquid, igniting charcoal or other carbonaceous matter.

Preparation.—

$Ba2ClO_3 + H_2SO_4$ (dil.) $= 2HClO_3 + \sqrt{BaSO_4}$

Reactions.—*θ.* $3HClO_3 = HClO_4 + H_2O + Cl_2 + 2O_2$

Forms chlorates, all of which are soluble and resemble nitrates.

Manufacture of Chlorate of Potash.

θ.
$$\left\{\begin{array}{rl} 6Ca2HO + 6Cl_2 &= Ca2ClO_3 + 5CaCl_2 + 6H_2O \\ Ca2ClO_3 + K_2CO_3 &= \sqrt{CaCO_3} + 2KClO_3 \end{array}\right.$$

PERCHLORIC ACID, $HClO_4$.—No anhydride known.

Preparation.—

θ. $2KClO_3 = KCl + KClO_4 + O_2$

Separate by crystallisation.

θ. $KClO_4 + H_2SO_4$ (dil.) $= 2HClO_4 + K_2SO_4$

TABLE XVII.

Action of SO_2 *on Acids of* Cl.

HClO, $HClO_2$, $HClO_3$ } reduced to HCl.

The others unacted upon.

PHOSGENE GAS, $COCl_2$.

Properties.—Colourless irritating gas. An acid chloride decomposed by H_2O.

$$COCl_2 + H_2O = CO_2 + 2HCl,$$

hence acid chloride of carbonic acid.

Preparation.—By direct union.

$$CO + Cl_2 = COCl_2$$

Reactions.—$4NH_3 + COCl_2 = CO2NH_2 + 2NH_4Cl$

Urea.

CARBON CHLORIDE, CCl_4.

Properties.—Colourless refractive liquid. Insoluble in water, soluble in alcohol and ether.

Preparation.—θ. $CS_2 + Cl_6 = CCl_4 + S_2Cl_2$

Separate by KHO, which dissolves the S_2Cl_2

Iodine.—I = 127.

Occurrence.—In sea water, sea weed, and certain springs, as NaI.

Properties.—Black metallic looking solid, slightly soluble in H_2O, more so in alcohol, and freely in ether.

Preparation.—From "kelp," the fused ash of seaweed. The kelp is heated with water, and the solution evaporated to separate out salts, the residue is distilled with MnO_2 and H_2SO_4:

θ. $2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + I_2$

Reactions.—Unites directly with some metals to form iodides. It is displaced from its combination by chlorine.

$$2KI + Cl_2 = 2KCl + I_2$$

It decomposes thiosulphate of soda in aqueous solution.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Tetrathionate of soda.

Unites with starch to form iodide of starch, which is *blue when cold, colourless when hot.*

Hydriodic Acid, HI.

Properties.—Colourless gas, soluble in water; solution unstable.

Preparation.—θ. $H_2 + I_2 = 2HI$

θ. $8H_2O + 5I_2 + P_2 = 10HI + 2H_3PO_4$

In aqueous solution $I_2 + H_2S = 2HI + \sqrt{S}$

Reactions.—$2HI + Cl_2 + 2HCl + I_2$

$2HI + 2Hg + Hg_2I_2 + H_2$

Forms iodides.

Manufacture of KI.

$$\left\{\begin{array}{c} 6KHO + 6I = 5KI + KIO_3 + 3H_2O \\ \theta.\ KIO_3 + 3C = KI + 3CO \end{array}\right\}$$

Iodic Anhydride, I_2O_5.

Properties.—White solid.
Preparation.—$\theta.\ 2HIO_3 = H_2O + I_2O_5$

Iodic Acid, HIO_3.

Preparation.—
$I_2 + 6HNO_3 = 2HIO_3 + 2H_2O + 2N_2O_3 + N_2O_4$.
Forms iodates, which are similar to chlorates.

Reactions.—$HIO_3 + 5HI = 3H_2O + 3I_2$
Periodic anhydride and acid, I_2O_4 and HIO_4. Corresponds to $HClO_4$, and prepared in the same manner.

Bromine.—Br = 80.

Occurrence.—Same as iodine, as $MgBr_2$
Preparation.—Same as iodine.
Properties.—Red fuming liquid, having similar properties to iodine as regards solubility.

Hydrobromic Acid, HBr.

Properties.—Colourless gas, soluble in water. Solution unstable.
Preparation.—Same as hydriodic acid.
Reactions.—$HBr + Cl = HCl + Br$
$\theta.\ HBr + H_2SO_4 = SO_2 + H_2O + Br$
Forms bromides.
Bromide of potassium, KBr, prepared in a similar manner to KI.

Hypobromous Anhydride and Acid.

Similar to hypochlorous anhydride and acid.

Bromic Acid.

Preparation.—$Ba2BrO_3 + H_2SO_4 = \sqrt{BaSO_4} + HBrO_3$

Fluorine.—Fl = 19.

Occurrence.—As $CaFl_2$
Preparation.—Not known.

Hydrofluoric Acid, HFl.

Preparation.—*θ.* $CaFl_2 + H_2SO_4 = 2HFl + CaSO_4$
Properties.—Colourless gas, condensible to a liquid. Soluble in water.
Reactions.—Dissolves all the metals except Pb, Ag, Pt, Au, and Mg. The dry gas has no action on glass, but if wet

$$4HFl + SiO_2 = 2H_2O + SiFl_4$$
A gas.

TABLE XVIII.

Review of Halogen Group.			
Cl	Br	I	Fl
HCl	HBr	HI	HFl
$HClO(Cl_2O)$	$HBrO-(Br_2O)$	—	—
$HClO_2(Cl_2O_3)$	—	—	—
— Cl_2O_4	—	—	—
$HClO_3$ —	$HBrO_3$ —	$HIO_3(I_2O_5)$	—
$HClO_4$ —		$HIO_4(I_2O_7)$	—

Sulphur.—S = 32.

Atomicity.—Dyad when united to basylous radicals.

Occurrence.—Free and combined in nature.

Properties.—Yellow solid. Allotropic and dimorphous. Three forms—(α.), (β.), and (γ.)

(α.) Octahedral crystals, soluble in CS_2

(β.) Prismatic crystals, soluble in CS_2, made by

(γ.) Action of heat on (α.)

Brown amorphous plastic mass, insoluble in CS_2, made by melting Sα or Sβ at a high temperature, and pouring into cold water. It is spontaneously transformed into S (α).

It unites directly with most of the metals, excepting Au, Pt, and Al. With Fe, Cu, Zn, and Sn, it unites with avidity.

It is inflammable, and burns in air to its lowest oxide, SO_2

Sulphuretted Hydrogen, H_2S.

(Sulphydric acid.)

Occurrence.—Free in nature, in certain springs, and in volcanic districts.

Properties.—Colourless gas with characteristic odour; very soluble in water; inflammable, burning in full supply of air to H_2O and SO_2

If air be insufficient it produces H_2O and $\sqrt{S}$

Preparation.—(*a.*) $FeS + H_2SO_4$ dil. $= H_2S + FeSO_4$

If strong H_2SO_4 be used the gas is decomposed.

$$H_2S + H_2SO_4 = 2H_2O + SO_2 + \sqrt{S}$$

(*b.*) $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$

θ. $H_2 + S = H_2S$

Reactions.—When passed through a tube heated above redness undergoes dissociation.

It is decomposed by most metals if heated:

i.e., *θ.* $Cu + H_2S = CuS + H_2$

$K_2 + H_2S = K_2S + H_2$

It converts oxides to sulphides:

$$CaO + H_2S = CaS + H_2O$$

It converts alkaline hydrates to sulphydrates:

$$KHO + H_2S = KHS + H_2O$$

On exposure to air these solutions turn yellow:

$$2KHS + O = K_2S_2 + H_2O$$

TABLE XIX.

Metallic Salts precipitated in Aqueous Solution by H_2S.

In acid solution—	In alkaline solution—
Au Pb As Sb	Fe Mn Zn *Cr
Pt Cu Cd	Ni *Al
Ag Sn	Co
Hg	

* These metals are thrown down as hydrates, the remainder as sulphides.

TABLE XX.

Special reactions of H_2S *in Aqueous Solution or suspended in Water.*

$$Fe_2Cl_6 + 2H_2S = FeCl_2 + 4HCl + \sqrt{S_2}$$
$$Fe_2O_3 + 3H_2S = 2FeS + 3H_2O + \sqrt{S}$$
$$4HNO_2 + 6H_2S = 2(NH_4NO_2) + 4H_2O + \sqrt{3S_2}$$
$$\left.\begin{matrix}Cl_2\\Br_2\\I_2\end{matrix}\right\} + H_2S = 2\left\{\begin{matrix}HCl\\HBr\\HI\end{matrix}\right. + \sqrt{S}$$
$$2CrO_3 + 3H_2S = \sqrt{Cr_2O_3} + 3H_2O + \sqrt{S_2}$$
$$N_2O_5 + 5H_2S = (NH_4)_2SO_4 + H_2O + \sqrt{2S_2}$$
$$SO_2 + 2H_2S = 2H_2O + 3S \text{ (Both gases dry).}$$
$$10SO_2 + 10H_2S = 2H_2S_5O_6 + 8H_2O + \sqrt{5S_2} \text{ in aqueous sol}^n.$$

Sulphides are formed in four ways:

(*a.*) By synthesis: θ. $Cu + S = CuS$

(*b.*) Reducing sulphates:

θ. $Na_2SO_4 + C = Na_2S + 4CO$

(*c.*) Boiling hydrates with sulphur.

(*d.*) By precipitation:

$Cu2NO_3 + H_2S = \sqrt{CuS} + 2HNO_3$

TABLE XXI.

Action of Heat on the Sulphides.

(*a.*) In Air.—All are decomposed, evolving SO_2 and leaving an oxide. The sulphides of Ag Pt and Hg leave the metals.

(*b.*) In Hydrogen.—
ZnS, MnS, FeS, Cu_2S, NiS = No action.
Au_2S_3, AgS_2, Bi_2S_3, Sb_2S_3 = H_2S and metals.

(*c.*) In Chlorine.—All are decomposed, forming chlorides and setting free sulphur.

Hydrosulphyl, H_2S_2.

Oily liquid, unstable.

Preparation.—$CaS_2 + 2HCl\ (dil.) = CaCl_2 + H_2S_2$

Sulphurous Anhydride, SO_2.

Properties.—Colourless gas, pungent smell. Soluble in water, with which it forms H_2SO_3

Reducing agent and bleacher:

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$$
$$N_2O_3 + SO_2 = SO_3 + 2NO$$

Preparation.—

(*a.*) *θ.* $S + O_2 = SO_2$

(*b.*) By boiling any heavy metal with concentrated H_2SO_4

θ. $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$

(*c.*) *θ.* $C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2$

(*d.*) By roasting sulphides in air.

Reaction.—Supports combustion of Fe, Sn, Pb, Zn, K, Na, producing sulphides and oxides.

θ. $2Zn + SO_2 = ZnS + 2ZnO$

PbO_2 is spontaneously inflammable in SO_2:

θ. $PbO_2 + SO_2 = PbSO_4$

Decomposed by nascent hydrogen:

$$3H_2 + SO_2 = 2H_2O + H_2S$$

Forms sulphites, the only soluble salts being those of the alkalies.

Action of Sulphites on Silver Salts.

$$*\theta.\begin{cases} K_2SO_3 + 2AgNO_3 = \overline{Ag_2SO_3} + 2KNO_3 \\ \overline{Ag_2SO_3} + H_2O = \overline{Ag_2} + H_2SO_4 \end{cases}$$

SULPHURIC ANHYDRIDE, SO_3.—White Solid.

Preparation.—Not by direct union, except through the agency of spongy platinum, then—

$$\theta.\ SO_2 + O = SO_3$$

By subliming it from Nordhausen, sulphuric acid, or from an anhydro-sulphate:

$$\left.\begin{array}{l} \theta.\ H_2SO_4SO_3 \\ \theta.\ Na_2SO_4SO_3 \\ \quad \text{or} \\ Na_2S_2O_7 \end{array}\right\} = \begin{array}{l} H_2SO_4 + SO_3 \\ \\ \\ Na_2SO_4 + SO_3 \end{array}$$

Properties.—White, silky crystals, with a strong affinity for water, with which it forms H_2SO_4 sulphuric acid.

* Compare this reaction with that of the thiosulphates.

Sulphuric Acid, H_2SO_4.

Nordhausen or Fuming Sulphuric Acid, $H_2SO_4SO_3$

Preparation.—By exposing iron pyrites to air, they undergo oxidation, forming $FeSO_4$

$2FeSO_4 + (air)\ O = Fe_2O2SO_4$, basic ferric sulphate.

This is next distilled, and the product received in ordinary H_2SO_4

$$\theta.\ Fe_2O2SO_4 = Fe_2O_3 + 2SO_3$$

Ordinary Sulphuric Acid, H_2SO_4.

Preparation.—(*a.*) $SO_3 + H_2O = H_2SO_4$

Chamber Process.

$$\left\{\begin{aligned} S + O_2 &= SO_2 \\ SO_2 + 2HNO_3 &= H_2SO_4 + N_2O_4 \\ 2H_2SO_3 + N_2O_4 &= 2H_2SO_4 + N_2O_2 \\ N_2O_2 + O_2 &= N_2O_4 \end{aligned}\right.$$

Sulphur or pyrites are burned in a current of air, and after mixing with nitric acid, evolved from $NaNO_3$ and H_2SO_4, is passed into leaden chambers, where the above actions take place. The acid so formed is concentrated first in leaden pans and afterwards in glass or platinum vessels.

Properties.—A dense, oily, acid liquid, having a strong affinity for water, decomposed at a high temperature.

$$\theta.\ H_2SO_4 = H_2O + SO_2 + O$$

TABLE XXII.

Action of Sulphuric Acid on Metals.

Strong.	*Dilute.*
$K = K_2SO_4 + H$	$K = K_2SO_4 + H$
$Na = Na_2SO_4 + H$	$Na = Na_2SO_4 + H$
$Ca = CaSO_4 + H$	$Ca = CaSO_4 + H$
$Ba = BaSO_4 + H$	$Ba = BaSO_4 + H$
Mg, Al, Zn, Fe, Ag, Ni, Co, Mn, Cu, Hg, Sn, Ci. No action in cold.	$Mg = MgSO_4 + H$
	$Al = Al_2 3SO_4 + H$
	$Zn = ZnSO_4 + H$
	$Fe = FeSO_4 + H$
	$Ni = NiSO_4 + H$
	$Co = CoSO_4 + H$
	$Mn = MnSO_4 + H$
If heated =	
$MgSO_4, Al_2 3SO_4, ZnSO_4, FeSO_4$	
$Ag_2SO_4, NiSO_4, CoSO_4, MnSO_4$	
$CuSO_4, HgSO_4, SnSO_4, Cr_2 3SO_4$	
and evolution of SO_2	
Au, Pt, and Bi no action.	Au, Pt, and Hg, Ag, Pb, } No action.
	Cu, Bi, & Sb = { No action if air be excluded.

TABLE XXIII.

Action of Sulphuric Acid on Acids.

$H_2C_2O_4 = H_2O + CO_2 + CO$	$HNO_2 = NO + HNO_3$
$H_2S = H_2O + SO_2 + S$	$H_2S_2O_3 = S + SO_2 + H_2O$
* { $H_4FeCy_6 = HCy$ if strong.	$HBr = Br + SO_2 + H_2O$
{ ,, $= CO$ if weak.	$HI = I + SO_2 + H_2O$
$HClO_3 = HClO_4 + Cl_2O_4$	

* (*a.*) $H_4FeCy_6 + 6H_2O + 6H_2SO_4 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4$

(*b.*) $2H_4FeCy_6 + 6H_2SO_4 + xH_2O = 6HCy + 6KHSO_4 + K_2Fe(FeCy_6) + xH_2O$

Action of Heat on the Sulphates.

Normal Sulphates of Alkalies.

No action.

Acid Sulphates of Alkalies.

Normal sulphate left, excess of acid, and water driven off:

i.e. $2KHSO_4 = K_2SO_4 + H_2O + SO_3$

Anhydro Sulphates of Alkalies.

Normal salt left, and excess of acid driven off:

i.e. $K_2SO_4, SO_3 = K_2SO_4 + SO_3$

Sulphates of Zn, Cd, Ni, Co, Mn @ red heat = No change
" " " above red heat = Oxide and SO_2 and O.

Sulphates of Sesquioxides of Iron Group.

Residue of oxide, and give off SO_3 and SO_2
All sulphates when heated with C = sulphide.

THIOSULPHURIC ACID, $H_2S_2O_3$.

(Hyposulphurous Acid.) A hypothetical acid forma set of salts thiosulphates. Most important salt, $Na_2S_2O_3$.

PREPARATION OF SODIUM THIOSULPHATE.

(*a.*) In aqueous solution, $Na_2SO_3 + S = Na_2S_2O_3$

(*b.*) $\left\{ \begin{array}{l} 2CaS + 2O_2 = CaS_2O_3 + CaO \\ CaS_2O_3 + Na_2CO_3 = \surd\overline{CaCO_3} + Na_2S_2O_3 \end{array} \right\}$

Properties.—White crystalline salt, soluble in H_2O

Reactions.—(See Iodine, page 28.)

On silver salts—

$$2AgNO_3 + Na_2S_2O_3 = \sqrt{\overline{Ag_2}}S_2O_3 + 2NaNO_3$$

The $Ag_2S_2O_3$ is soluble in excess of $Na_2S_2O_3$ forming $NaAgS_2O_3$

If $Ag_2S_2O_3$ be boiled,

$$Ag_2S_2O_3 + H_2O = \sqrt{\overline{Ag_2}}S + H_2SO_4$$

All the haloid salts of silver are soluble in aqueous solution of $Na_2S_2O_3$

The thiosulphates are all decomposed by acids :

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + \sqrt{\overline{S}} + SO_2$$

Hyposulphurous Acid, H_2SO_2.

Also called hydrosulphurous acid.

Preparation.—$Zn + H_2SO_3 = ZnO + H_2SO_2$

Properties.—Yellow, unstable liquid, having a strong affinity for oxygen. Powerful bleacher.

The higher acids of sulphur are called Thionic Acids, with a prefix denoting the quantity of S they contain.

Di	— thionic	$H_2S_2O_6$
Tri	— ,,	$H_2S_3O_6$
Tetra	— ,,	$H_2S_4O_6$
Penta	— ,,	$H_2S_5O_6$

Carbon Disulphide, CS_2.

Preparation.—θ. $S_2 + C = CS_2$

Properties.—Mobile colourless liquid, having peculiar odour, not miscible with water. Inflammable, burning to CO_2 and SO_2 with a pale blue flame. It is decomposed by potassium in a similar way to CO_2

$$\theta.\ 2K_2 + CS_2 = 2K_2S + C$$

Reactions.—(*a.*) On aqueous solutions of hydrates:

$$6KHO + 3CS_2 = \underset{\text{Sulpho-Carbonate.}}{2K_2CS_3} + K_2CO_3 + 3H_2O$$

(*b.*) If hydrate be heated and CS_2 vapour passed over it:

$$\theta.\ 2Ca2HO + CS_2 = 2CaO + CO_2 + 2H_2S$$

(*c.*) With sulphides:

$$K_2S + CS_2 = K_2CS_3$$

(*d.*) With alcoholic ammonia:

$$CS_2 + 2NH_3 = \underset{\text{Sulpho-Cyanate.}}{NH_4CNS} + H_2S$$

Sulphur and Chlorine.

Subchloride most common, S_2Cl_2.

Preparation.—$\theta.\ S_2 + Cl_2 = S_2Cl_2$

Properties.—Reddish mobile liquid, decomposed by water.

$$2S_2Cl_2 + 3H_2O = 4HCl + SO_2 + H_2O + 3S$$

Dichloride, SCl_2.

Preparation.—By using excess of chlorine.

Properties.—Decomposed by light and water.

Chloride of Sulphuryl, SO_2Cl_2.

Preparation.—(*a.*) Direct union of SO_2 and Cl_2 in sunlight.

(*b.*) *θ.* $H_2SO_4 + 2PCl_5 = 2POCl_3 + 2HCl + SO_2Cl_2$

Properties.—Colourless fuming liquid, decomposed by water.

$$SO_2Cl_2 + 2H_2O = 2HCl + H_2SO_4$$

Chloride of Thionyl, $SOCl_2$.

Preparation.—$SO_2 + PCl_5 = POCl_3 + SOCl_2$

Properties.—Colourless refractive liquid, decomposed by water.

$$SOCl_2 + 2H_2O = 2HCl + H_2O + SO_2$$

Selenium and Tellurium are unimportant.

Phosphorous.—P = 31 Triad and Pentad.

An allotropic element.

Occurrence.—Never native, always in combination, generally with lime, as Ca_32PO_4

Preparation.—(*a.*) Yellow crystalline variety. Bone ash dissolved in H_2SO_4

$$Ca_32PO_4 + 2H_2SO_4 = 2CaSO_4 + CaH_42PO_4$$

The $CaSO_4$ is separated, and the superphosphate of lime, CaH_42PO_4 is heated.

$$\theta.\ CaH_42PO_4 = Ca2PO_3 + 2H_2O$$

The metaphosphate of lime is distilled with carbon.

$$\theta.\ 3Ca2PO_3 + C_{10} = Ca_32PO_4 + 10CO + P_4$$

or

$$\theta.\ 2Ca2PO_3 + 2SiO_2 + 5C_2 = 2CaSiO_3 + 10CO + P_4$$

(*b.*) *Amorphous Phosphorous. Red Phosphorous.*

By acting on yellow phosphorous at a temperature of 230° C. to 245° C. for at least thirty hours.

Properties.—(*a.*). *Yellow.*

Yellow crystalline solid, usually in sticks; soluble in bisulphide of carbon, oil, and turpentine, very poisonous and inflammable, burning to P_2O_5. It has a great affinity for oxygen, and to prevent spontaneous ignition is kept under water.

(*b.*) *Red.*—An amorphous red powder, which is neither soluble in CS_2 nor poisonous; it is not combustible until converted into the yellow form, which it can be at a temperature above 248° C.

Phosphuretted Hydrogen.

Three forms:

(*a.*) Gaseous, PH_3

Preparation.—$\theta.\ 2HPH_2O_2 = H_3PO_4 + PH_3$

$\theta.\ 3NaHO + P_4 + 3H_2O = 3NaH_2PO_2 + PH_3$

Properties.—Gas with characteristic odour; inflammable, burning to H_3PO_4. Unites under pressure with HCl to form PH_4Cl, phosphonium chloride. It decomposes aqueous solutions of metallic salts.

$$2PH_3 + 3CuSO_4 = \sqrt{Cu_3P_2} + 3H_2SO_4$$

$$PH_3 + 8AgNO_3 + 4H_2O = \sqrt{4Ag_2} + H_3PO_4 + 8HNO_3$$

(*b.*) Liquid, P_2H_4

Preparation.—$Ca_2P_2 + 4H_2O = P_2H_4 + 2(Ca2HO)$

Properties.—Spontaneously inflammable.

(*c.*) Solid, P_4H_2

Preparation.—If HCl be used instead of H_2O, then the solid compound is obtained.

PHOSPHOROUS OXIDES AND ACIDS.

Phosphorous Anhydride, P_2O_3.

Preparation.—By combustion of phosphorous in a limited supply of O.

Properties.—White deliquescent solid, oxidizable; unites with water to form H_3PO_3, phosphorous acid.

Phosphorous Acid, H_2PHO_3, not H_3PO_3.

As only two atoms of hydrogen are displaceable, it is thus a dibasic acid.

Preparation.—By passing chlorine through phosphorous melted under hot water.

$$PCl_3 + 3H_2O = H_2PHO_3 + 3HCl$$

Properties.—White deliquescent crystals, unstable.

Phosphoric Anhydride, P_2O_5.

Preparation.—By direct union.

$$\theta.\ P_2 + O_5 = P_2O_5$$

Properties.—White deliquescent solid. Unites with water to form three distinct acids.

$P_2O_5 + H_2O = 2HPO_3$ metaphosphoric acid.
$P_2O_5 + 2H_2O = H_4P_2O_7$ pyro „ „
$P_2O_5 + 3H_2O = 2H_3PO_4$ ortho „ „

Metaphosphoric Acid, HPO_3.

Preparation.—By heating glacial phosphoric acid to redness.

Metaphosphates made by heating the dihydrogen phosphate.

$$\theta.\ NaH_2PO_4 = NaPO_3 + H_2O$$

Pyrophosphoric Acid, $H_4P_2O_7$.

Preparation.—$Pb_2P_2O_7 + 2H_2S = \sqrt{2PbS} + H_4P_2O_7$

Pyrophosphates are made by heating monohydrogen phosphates.

$$\theta.\ 2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

Orthophosphoric Acid.

Preparation.—

(*a.*) $\theta.\ 3P_4 + 20HNO_3 + 8H_2O = 12H_3PO_4 + 20NO$

(*b.* $CaH_42PO_4 + H_2SO_4 = \sqrt{CaSO_4} + 2H_3PO_4$

Preparation of Phosphates of Soda.

If phosphoric acid is added to sodic hydrate until alkaline reaction be gone, or if sodic hydrate be added to phosphoric acid until acid reaction be gone, we have Na_2HPO_4 in solution.

$$H_3PO_4 + 2NaHO = Na_2HPO_4 + 2H_2O.$$

This is common phosphate of soda, usually made in following manner:

$$CaH_42PO_4 + Na_2CO_3 = \downarrow CaHPO_4 + Na_2HPO_4 + CO_2 + H_2O$$

Preparation of Dihydrogen Phosphates.

$$Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4.$$

Preparation of Trisodic Phosphate.

$$Na_2HPO + NaHO = Na_3PO_4 + H_2O.$$

This salt is unstable, and is decomposed by water gradually.

TABLE XXIV.

Action of Heat on Phosphates of Soda and Ammonia.

(1.) Na_3PO_4	= nil.
(2.) $2Na_2HPO_4$	= $Na_4P_2O_7 + H_2O$
(3.) NaH_2PO_4	= $NaPO_3 + H_2O$
(1.) $(NH_4)_3PO_4$	= No Salt of this formula.
(2.) $(NH_4)_2HPO_4$	= $NH_3 + H_3PO_4$
(3.) $NH_4H_2PO_4$	
(4.) NH_4HNaPO_4 Microcosmic salt.	= $NH_3 + H_2O + NaPO_3$

HYPOPHOSPHOROUS ACID, HPH_2O_2 (H_3PO_2).

Preparation.—

$$\theta. \begin{cases} 3(Ba2HO) + 2P_4 + 6H_2O = 3Ba2PH_2O_2 + 2PH_3 \\ Ba2PH_2O_2 + H_2SO_4(\text{dil.}) = \downarrow BaSO_4 + 2H_3PO_2 \end{cases}$$

Properties.—Great reducing agent, tends to become H_3PO_4

θ. $KH_2PO_2 + 2KHO = K_3PO_4 + 2H_2$

Action of Heat on Hypophosphites.

$$5NaH_2PO_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2$$

CHLORIDES OF PHOSPHOROUS.

Phosphorous Chloride, PCl_3.

Preparation.—By direct union with phosphorous in excess.

Properties.—Colourless volatile liquid.

Reactions.—$PCl_3 + 3H_2O = 3HCl + H_3PO_3$

Phosphoric Chloride, PCl_5.

Preparation.—By direct union with chlorine in excess.

Properties.—Solid crystalline compound.

Reactions.—(*a.*) $PCl_5 + H_2O = POCl_3 + 2HCl$
(*b.*) $PCl_5 + 4H_2O = 5HCl + H_3PO_4$

Sulphur and phosphorous unite directly to form several sulphides.

Boron.—B = 11 Triad.

An allotropic element.

Occurrence.—Never native; always combined as borates, as boracic acid, or sulphide of boron.

Preparation.—

(*a.*) Amorphous.—Green powder, burns in air to B_2O_3

θ. $B_2O_3 + 3Na_2 = 3Na_2O + B_2$

(*b.*) Diamond.—Colourless crystals.

$Al_2 + B_2O_3 = Al_2O_3 + B_2$

(*c.*) Graphitoidal.—Dark crystalline plates.

$2BFl_3 + Al_2 = Al_2Fl_6 + B_2$

Boric Oxide or Boracic Anhydride.

Preparation.—θ. $2H_3BO_3 = B_2O_3 + 3H_2O$

Properties.—A white glassy substance, soluble in water, and, when fused, having the property of dissolving metallic oxides.

Boric or Boracic Acid, H_2BO_3.

Occurrence.—Free in lagoons of Tuscany, formed in probability by the following reaction :

$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S$

Preparation.—

(*a.*) By evaporation of watery solution obtained from the lagoons.

(*b.*) By acting on borax with sulphuric acid.

$2NaBO_2.B_2O_3 + H_2SO_4 + 5H_2O =$
$4H_3BO_3 + Na_2SO_4$

Properties.—White crystalline scales, not freely soluble in water; volatile in presence of steam, but fixed when anhydrous.

BORON NITRIDE, BN.

Preparation.—By direct union.
Reaction.—$2BN + 3H_2O = 2NH_3 + B_2O_3$

BORON SULPHIDE, B_2S_3.

Preparation.—*θ.* $2B_2O_3 + 3C + 3CS_2 = 2B_2S_3 + 6CO$

BORON CHLORIDE, BCl_3, Liquid.

$2Cl_3 + B_2O_3 + C_3 = 2BCl_3 + 3CO$

Decomposed by water—

$BCl_3 + 3H_2O = H_3BO_3 + 3HCl$

BORON FLUORIDE, BFl_3, Colourless gas.

Preparation.—

$B_2O_3 + 3CaFl_2 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BFl_3$

Decomposed by water—

$4BFl_3 + 3H_2O = H_3BO_3 = 3BFl_3HFl$
Hydrofluoboric acid.

Silicon.—Si = 28·5 Tetrad.

Allotropic element, analogous to carbon.

Occurrence.—Combined as silica, SiO_2, and as silicates.

Preparation.—

(*a.*) Amorphous.—Brown powder.

$SiFl_4\,(NaFl)_4 + 2Na_2 = 6NaFl + Si$
Silico fluoride.

(*b.*) Graphitoidal.—If amorphous silicon be fused with aluminium, silicon in the form of dark crystalline plates is obtained.

(*c.*) Diamond.—Colourless crystals.

θ. $3SiCl_4 + 2Al_2 = 2(Al_2Cl_6) + 3Si$

Silicic Hydride, SiH_4.

Preparation.—$SiMg_2 + 4HCl = 2MgCl_2 + SiH_4$

Properties.—Colourless gas, spontaneously inflammable; burns with white flame to SiO_2 and H_2O

Silica, SiO_2.

Occurs free as sand and quartz, and combined as silicates.

Forms two acids—H_2SiO_3, gelatinous silicic acid; and H_4SiO_4, soluble silicic acid.

Glass.—(*a.*) Soluble. Made by heating flints and sodic hydrate together under pressure.

(*b.*) Ordinary glass consists of double silicates of alkaline and other metals.

Silicon Chloride, $SiCl_4$.

Preparation.—*θ.* $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$

N.B.—No action if the carbon be omitted.

Properties.—Colourless volatile liquid, decomposed by water.

$$SiCl_4 + 2H_2O = 4HCl + \sqrt{SiO_2}$$

Silicon Fluoride, $SiFl_4$.

Preparation.—

θ. $2CaFl_2 + SiO_2 + 2H_2SO_4 = SiFl_4 + 2CaSO_4 + 2H_2O$

Properties.—Colourless gas, acted on by water as under:

$$3SiFl_4 + 4H_2O = \sqrt{H_2SiO_3} + 2(2HFl.SiFl_4) + H_2O$$

Hydrofluosilicic Acid.

Hydrofluosilic Acid, $2HFl.SiFl_4$.

Preparation.—As above.

Properties.—Colourless acid liquid, decomposed on concentration into $SiFl_4$ and $2HFl$

Reactions.—

Small quantity of KHO—

$$2HFl.SiFl_4 + 2KHO = \sqrt{2KFl.SiFl_4} + 2H_2O$$

Excess of KHO—

$$2HFl.SiFl_4 + 6KHO = \sqrt{SiO_2} + 6KFl. + 4H_2O$$

Silicic Sulphide, SiS_2.

Preparation.—*θ.* $SiO_2 + CS_2 = SiS_2 + CO_2$

METALLIC ELEMENTS.

First Group.—Alkaline Metals, K,Na,NH_4.

General Characters.—All monads. Decompose water at ordinary temperature. Oxidizable, having to be kept under mineral naphtha. Their hydrates, oxides, carbonates and phosphates are soluble. Their carbonates and hydrates are not decomposed by heat.

Potassium.—K = 39.

Occurrence.—In plant ashes as carbonate. As sulphate (kainet) and chloride in Prussia. As bitartrate in argol. As silicate in certain minerals, such as felspar, &c.

Preparation.—(*a.*) *θ.* $K_2CO_3 + 2C = 3CO + K_2$

(*b.*) Electrolysis of KHO or KCl.

Oxides, K_2O, K_2O_2, K_2O_4.—The first is the only basic oxide.

Preparation.—*θ.* $2KHO + K_2 = 2K_2O + H_2$

Properties.—White deliquescent solid.

Hydrate.

Preparation.—

θ. In aqueous solution, $K_2CO_3 + Ca2HO = \sqrt{CaCO_3} + 2KHO$

Properties.—White deliquescent solid.

CARBONATE.

Preparation.—By purifying wood ashes, or by ignition of bitartrate.

BICARBONATE.

Preparation.—$K_2CO_3 + H_2O + CO_2 = \sqrt{2KHCO_3}$

The other salts have been already referred to, or do not call for special notice.

Sodium.—Na = 23.

Occurrence.—Chiefly as chloride, NaCl, and nitrate, $NaNO_3$

Preparation.—Similar to potassium.

OXIDES.—Two, Na_2O (basic) and Na_2O_2

HYDRATE.—Prepared like potassium hydrate.

CARBONATE—SALT CAKE PROCESS.

$$\theta.\ \begin{cases} 2NaCl + H_2SO_4 = NaHSO_4 + HCl \\ NaHSO_4 + NaCl = Na_2SO_4 + HCl \end{cases}$$

The sulphate thus prepared is mixed with coal and limestone, and again heated, when the following reactions occur:

$$\theta.\ Na_2SO_4 + 4C = Na_2S + 4CO$$

$$\theta.\ Na_2S + CaCO_3 = \underset{\text{Soluble.}}{Na_2CO_3} + \underset{\text{Insoluble.}}{CaS}$$

Dissolve out the carbonate and crystallise.

BICARBONATE.—By passing CO_2 over the crystallised carbonate.

TABLE XXV.

Special Reactions of Solution of Na_2CO_3.

$Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = \sqrt{Fe_2 6HO} + 6NaCl + 3CO_2$

$Al_2Cl_6 + 3Na_2CO_3 + 3H_2O = \sqrt{Al_2 6HO} + 6NaCl + 3CO_2$

$4MgSO_4 + 4Na_2CO_3 + H_2O = \sqrt{3MgCO_3.Mg2HO} +$
or any soluble salt. $4Na_2SO_4 + CO_2$

$3ZnSO_4 + 3Na_2CO_3 + 2H_2O = \sqrt{ZnCO_3.2(Zn2HO)} +$
or any soluble salt. $3Na_2SO_4 + 2CO_2$

BORATE or BORAX, $Na_2O2B_2O_3$, found native as tincal, also—

Prepared by neutralising Na_2CO_3 with H_3BO_3
The other salts described elsewhere.

Ammonium.—NH_4.

Hypothetical metal, never yet isolated.

Ammonium Amalgam.—A concentrated solution of NH_4Cl is poured on sodium amalgam, when an interchange is supposed to take place, chloride of sodium being formed, and the ammonium uniting with the mercury to form an unstable amalgam.

HYDRATE, NH_4HO.

Preparation.—By passing NH_3 gas into water.

CHLORIDE.—(Sal. ammoniac) NH_4Cl

Preparation.—

θ. $(NH_4)_2SO_4 + 2NaCl = Na_2SO_4 + 2NH_4Cl$

CARBONATE.—Ordinary smelling salts is a mixture of carbonate and carbamate.

Preparation.—

θ. $3\,(NH_4)_2SO_4 + 3CaCO_3 = (NH_4NH_2CO_2.2NH_4HCO_3) + 2NH_3 + 3CaSO_4$

It decomposes when dissolved in water,

$$NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3$$

GROUP II.—METALS OF ALKALINE EARTHS.

Ba, Sr, Ca.

General Characters.—All decompose water at ordinary temperature; all are prepared by the electrolysis of the fused chlorides; they are oxidizable, having to be kept under mineral naphtha. Their hydrates and oxides are only slightly soluble in water. The hydrates are decomposed by heat. They are all dyads. Their carbonates, sulphates, phosphates are insoluble,

Barium.—Ba = 137.

Occurrence.—As sulphate = (heavy spar).
Carbonate = (witherite).

Preparation.—(See general characters.)

Oxides.—BaO and BaO_2. The first is basic.

BaO. *Preparation.*—*θ.* $Ba2NO_3 = BaO + N_2O_4 + O$

BaO_2. *Preparation.*—*θ.* $BaO + O = BaO_2$

HYDRATE, Ba2HO.

Preparation.—(*a.*) $BaO + H_2O = Ba2HO$

(*b.*) $BaCl_2 + 2NaHO = Ba2HO + 2NaCl$

CHLORIDE.

Preparation.—(*a.*) From witherite:

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$$

(*b.*) From heavy spar:

$$\theta. \begin{cases} BaSO_4 + 4C = BaS + 4CO \\ BaS + 2HCl = H_2S + BaCl_2 \end{cases}$$

NITRATE, $Ba2NO_3$.

Preparation.—(*a.*) From witherite:

$$BaCO_3 + 2HNO_3 = Ba2NO_3 + CO_2 + H_2O$$

(*b.*) From heavy spar:

$$\theta. \begin{cases} BaSO_4 + 6C = BaS + 4CO \\ BaS + 2HNO_3 = Ba2NO_3 + H_2S \end{cases}$$

Calcium.—Ca = 40.

Occurrence.—As carbonate in limestone, coral, Iceland spar, calcite, chalk, marble, &c.

OXIDE, CaO.—By heating limestone, $CaCO_3$

HYDRATE.—The oxide unites with water, evolving great heat, producing the hydrate Ca2HO. This phenomenon is called "slaking." Setting of mortar due to formation of carbonate. Setting of cement due to formation of silicate.

SULPHATE, $CaSO_4$.

Occurrence.—Native as gypsum, $CaSO_4 2H_2O$, and selenite.

Properties.—On heating, the gypsum loses the two molecules of water, and is now termed "plaster of Paris;" when this plaster "sets," it takes up these two molecules again.

CHLORIDE, $CaCl_2$.

Preparation.—$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$
When fused, used for drying gases.

Strontium.—Si = 87·6.

Occurrence.—As carbonate (celestine).
As sulphate.

The salts are similar to those of Barium, but unimportant. The nitrate and chloride are prepared from the sulphate in a similar manner to the barium compounds.

GROUP III.—METALS OF THE IRON GROUP.

Sub-Group, Mg, Zn, and Cd.

General Character.—They are all dyads, and form isomorphous salts. They are volatile and combustible, and form only one oxide, which is insoluble.

Magnesium.—Mg = 24.

Occurrence.—As chloride in sea water. As dolomite ($MgCO_3CaCO_3$), steatite or silicate, meerschaum (silicate), &c.

Preparation—By (*a.*) electrolysis of fused chloride.

$$\theta.\ (b.)\ MgCl_2 + Na_2 = 2NaCl + Mg$$

Properties.—Silver white metal, decomposing boiling water slowly, and an aqueous solution of NH_4Cl quickly.

$$\theta.\ 4NH_4Cl + Mg = 2NH_4Cl.MgCl_2 + 2NH_3 + H_2$$

Fuses at red heat, and burns in air to form MgO

OXIDE, MgO.—White powder.

Preparation.—By heating the carbonate.

CHLORIDE, $MgCl_2$.—White deliquescent solid.

Preparation.—$MgCO_3 + 2HCl = MgCl_2 + H_2O$.

Properties.—When once in solution, cannot be recovered by simple evaporation, as the following decomposition occurs:

$$\theta.\ MgCl_2 + H_2O = MgO + 2HCl$$

To overcome this difficulty the solution is mixed with NH_4Cl; it can then be evaporated, leaving a double salt, $2NH_4Cl.MgCl_2$; on heating this the ammonium salt is volatilised.

CARBONATE, $MgCO_3$.—White insoluble powder.

Preparation.—

$$4MgSO_4 + 4Na_2CO_3 + H_2O = \sqrt{3MgCO_3.Mg2HO} + 4Na_2SO_4 + CO_2$$

SULPHATE, $MgSO_4$ (Epsom Salts).

Occurs native in certain springs.

Preparation.—

$$\underset{\text{Dolomite.}}{MgCO_3CaCO_3} + 2H_2SO_4 = \underset{\text{Insoluble.}}{CaSO_4} + \underset{\text{Soluble.}}{MgSO_4} + 2CO_2 + 2H_2O$$

SULPHIDE.

Preparation.—θ. (*a.*) $MgSO_4 + 4C = MgS + 4CO$

θ. (*b.*) $2MgO + C + CS_2 = 2MgS + 2CO$

Zinc.—Zn = 65·2.

Occurrence.—As blende, ZnS, and calamine, $ZnCO_3$

Metallurgy.—The ore is roasted, and thus converted into oxide. This is then distilled with carbon:

$$\theta.\ ZnO + C = CO + Zn$$

Properties.—Bluish white metal, crystalline and brittle; if heated, it becomes malleable. Burns in air with a green flame to oxide. Alloyed with Ni = German silver.

OXIDE, ZnO.—White powder, powerful base.

Preparation.—By ignition of carbonate.

CHLORIDE, $ZnCl_2$.—White, amorphous, deliquescent solid.

Preparation.—$Zn + 2HCl = ZnCl_2 + H_2$

$ZnO + 2HCl = ZnCl_2 + H_2O$

$ZnCO_3 + 2HCl = ZnCl_2 + H_2O + CO_2$

SULPHATE, $ZnSO_4$ (White Vitriol).—White crystalline solid.

Preparation.—$Zn + H_2SO_4 = ZnSO_4 + H_2$

CARBONATE.—White amorphous powder.

Preparation.—Occurs native, or made by precipitation.

$3ZnSO_4 + 2H_2O + 3Na_2CO_3 = \sqrt{ZnCO_3 2(Zn2HO)}. + 2CO_2 + 3Na_2SO_4$

Cadmium.—Cd = 112.

Occurrence.—With zinc ores. It is much more volatile than zinc, and distils over first. In appearance and general properties it has a strong resemblance to zinc. The sulphide and iodide are the most important salts—the former being made by precipitation, the latter by direct union.

ALUMINIUM.—*Sub-Group.*

Al, Fe, Mn, Cr.

General Characters.—With the exception of aluminium, they form four oxides, two of which are basic, one neutral, and one acid. Their chief oxides are sesquioxides. They all form double sulphates with the alkaline metals, which crystallise with $24H_2O$, and are called alums.

TABLE XXVI.

Ous.	FeO	MnO	CrO	—
Ic.	Fe_2O_3	Mn_2O_3	Cr_2O_3	Al_2O_3
Ous-Ic.	Fe_3O_4	Mn_3O_4	Cr_3O_4	—
Acid.	FeO_3	MnO_3	CrO_3	—
Alums.	$K_2Fe_24SO_4$	$K_2Mn_24SO_4$,	$K_2Cr_24SO_4$	$K_2Al_24SO_4$

Aluminium.—Al = 27·5.

Occurrence.—Clay, felspar, marl, granite (*silicates*).

Preparation.—Clay, &c. is fused with NaHO when sodic aluminate is formed, $Na_2Al_2O_4$. This is dissolved in water and decomposed by CO_2, when $\surd\overline{Al_2}6\overline{HO}$ (hydrate) is produced. This is dried, mixed with coal and salt, and heated in a current of chlorine, when Al_2Cl_6 is produced. The following equation shows the remainder of the process:

$$\theta.\ Al_2Cl_6 + 6Na = 6NaCl + Al_2$$

Properties.—Brilliant white metal, not readily tarnished; very light; soluble in most acids, and in alkaline hydrates; alloyed with 90% Cu = Aluminium gold.

OXIDE, Al_2O_3.—Found native in an impure condition as corundum and emery. White amorphous powder.

Preparation.—

(*a.*) $\left\{\begin{array}{l} Al_2 3SO_4(NH_4)_2SO_4 + 6NH_4HO = \sqrt{Al_2 6HO} + 4(NH_4)_2SO_4 \\ \theta.\ Al_2 6HO = Al_2O_3 + 3H_2O \end{array}\right.$

(*b.*) $\theta.\ Al_2 3SO_4(NH_4)_2SO_4 = Al_2O_3 + (NH_4)_2SO_4 + 3SO_3$

The ammonic sulphate and sulphuric anhydride volatilise.

The hydrate has the power of uniting with certain colouring matters to form a "lake," hence the use of alum as a mordant in dyeing.

CHLORIDE, Al_2Cl_6.—White, amorphous, deliquescent solid, which, when in solution, cannot be recovered by evaporation, decomposition occurring in a similar manner to the magnesium chloride. It is volatile.

Preparation.—$\theta.\ Al_2O_3 + C_3 + Cl_6 = Al_2Cl_6 + 3CO$

Action of aqueous Na_2CO_3 on solution by Al_2Cl_6:

$$Al_2Cl_6 + 3Na_2CO_3 + 3H_2O = \sqrt{Al_2}6HO + 6NaCl + 3CO_2$$

SULPHATE, $Al_2 3SO_4$.—White amorphous mass.

Preparation.—By heating clay with H_2SO_4

Alums.

Common alum, $Al_2 3SO_4 K_2SO_4$ or $Al_2 3SO_4(NH_4)_2 SO_4$, is usually prepared from alum shale, which consists of clay, coaly matter (*bitumen*), and iron pyrites. This substance is exposed in heaps to the action of the air, when the sulphur of the pyrites is oxidized to sulphuric acid, which combines with the iron to form $FeSO_4$, and decomposes the clay, setting free silica and forming $Al_2 3SO_4$. The soluble constituents are washed out and the liquor evaporated with KCl, or gas liquor, when either potassium or ammonium alum crystallise out.

The other alums are prepared by dissolving the sesquioxide of their respective metals in dilute sulphuric acid, and crystallising with a sulphate of an alkaline metal.

Actions of aqueous Na_2CO_3 on solution of alum:

$$Al_2 3SO_4.K_2SO_4 + 3H_2O + 3Na_2CO = \sqrt{Al_2 6HO} + K_2SO_4 + 3Na_2SO_4 + 3CO_2$$

If a smaller quantity of carbonate be used the precipitate at first formed redissolves, and there is then in solution basic sulphate of alumina:

$$Al_2 3SO_4.K_2SO_4 + 2Na_2CO_3 = Al_2O_2SO_4 + 2Na_2SO_4 + K_2SO_4 + 2CO_2$$

If the solution be now boiled:

$$\theta.\ 3Al_2O_2SO_4 + K_2SO_4 + xH_2O = \sqrt{2Al_2O_3} + Al_2 3SO_4.K_2SO_4 + xH_2O$$

Iron, Fe = 56.

Occurrence.—Rarely native—chiefly as oxide. Fe_2O_3 (*red hæmatite*), $Fe_2O_3H_2O$ (*brown hæmatite*), Fe_3O_4 (*magnetic oxide*), $FeCO_3$, with clay (*clay ironstone*), FeS_2, iron pyrites. The latter is not worked for metal.

Preparation.—Ore first roasted, by which operation it is converted into oxide, and then smelted with coal and limestone in a blast furnace.

TABLE XXVII.

Chemical Changes in the Blast Furnace.

From below upwards.

1. Air + C = CO_2
2. CO_2 + C = 2CO
3. 3CO + Fe_2O_3 = 3CO_2 + Fe_2

If ore were pure, process might be stopped here, but being mixed with the clay, and pure iron being infusible, the following reactions are necessary :—

4. Fe + C = cast iron (*fusible*).
5. Clay + CaO = fusible slag.

Purification of Cast Iron.—Puddling.

The crude iron is melted in a furnace with oxide of iron, sand, and lime. The carbon and silicon are removed as oxides, and the phosphorous and sulphur washed out by the silicates. The purified metal is then rolled, and forms bar iron (*wrought iron*).

STEEL is prepared in two ways:

1*st*. By heating wrought iron with charcoal for a lengthened period.

2*d*. By the BESSEMER PROCESS.

This process is conducted as follows:—The iron is melted and air forced through, by which the carbon is oxidized and removed as CO; enough cast iron is then added to supply the necessary quantity of carbon to convert the whole into steel. The carbon in steel is chiefly in the combined state, whereas in cast iron it is largely in the free condition (*graphitoidal*).

Properties.—Pure metal is white and lustrous. In commerce three varieties are met with, viz., wrought, cast, and steel. Hammered iron has a crystalline, and rolled iron a fibrous structure. It is the most magnetic of the metals, and is unchanged in dry air or pure water, provided that the latter contains no free oxygen or carbonic acid.

OXIDES OF IRON.

FERROUS OXIDE, FeO.—Almost unknown in pure state. It is a powerful base, and its salts are usually of a pale green colour.

Preparation.—$FeSO_4 + 2KHO = \sqrt{Fe2HO} + K_2SO_4$

FERRIC OXIDE, Fe_2O_3.—Found native. Red powder.

Prep.— $\left\{\begin{array}{l} Fe_23SO_4 + 6KHO = \sqrt{Fe_26HO} + 3K_2SO_4 \\ \theta. \quad Fe_26HO \qquad\quad = \quad Fe_2O_3 \quad + 3H_2O \end{array}\right.$

FERROUS FERRIC OXIDE.—Black powder.

Preparation.—(*a.*) $\theta.\ 3Fe + 4H_2O = Fe_3O_4 + 4H_2$

(*b.*) $\theta.\ 3Fe + 2O_2 = Fe_3O_4$

FERRIC ANHYDRIDE, FeO_3, forming ferric acid, H_2FeO_4

Both unknown in the free condition. Ferrate of potassium prepared as follows:—

$$Fe_2O_3 + 10KHO + 3Cl_2 = 6KCl + 5H_2O + 2K_2FeO_4$$

Very unstable, and decomposed in presence of water.

$$2K_2FeO_4 + 4H_2O = 2KHO + \sqrt{Fe_2 6HO} + 2O_2$$

CHLORIDES.

FERROUS, $FeCl_2$

Preparation.—$Fe + 2HCl = FeCl_2 + H_2$

FERRIC, Fe_2Cl_6

Preparation.—(*a.*) $FeCl_2 + 2Cl_2 = Fe_2Cl_6$ (in aqueous solution).

(*b.*) $6FeCl_2 + 6HCl + 2HNO_3 = 3Fe_2Cl_6 + 2NO + 4H_2O$

SULPHATES.

FERROUS, $FeSO_4$ (Green Vitriol).

Preparation.—$Fe + H_2SO_4 = FeSO_4 + H_2$

A solution of ferrous sulphate, if exposed to air, turns brown, owing to formation of basic ferric sulphate, Fe_2O2SO_4

$$2FeSO_4 + O = Fe_2O2SO_4$$

The constitution of this salt is shown by the constitutional formula:

$$Fe_2\begin{cases} SO_4 \\ SO_4 \\ SO_4 \end{cases}$$

Ferric sulphate.

$$Fe_2\begin{cases} SO_4 \\ O \\ SO_4 \end{cases}$$

Basic ferric sulphate.

FERRIC, $Fe_2 3SO_4$

Preparation.—$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = (Fe_2 3SO_4) + 2NO + 4H_2O$

CARBONATE.—Only one known, $FeCO_3$.

Preparation.—

$$FeSO_4 + (NH_4)_2CO_3 = \sqrt{FeCO_3} + (NH_4)_2SO_4$$

If a soluble carbonate be added to an aqueous solution of a ferric salt, the following change takes place:

$$Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = \sqrt{Fe_2}6HO + 6NaCl + 3CO_2$$

SULPHIDE, FeS.—Made by direct union.

FERRO AND FERRID CYANIDES OF IRON.—(*See* CYANOGEN.)

Manganese.—Mn = 55.

Occurrence.—Mn_2O_3 (*braunite*), $Mn_2O_3H_2O$ (*manganite*), Mn_3O_4 (*hausmannite*), MnO_2 (*pyrolusite*).

Preparation.—By strong ignition of MnO_2 in crucible of lime.

Properties.—Greyish white metal, which slowly decomposes water.

OXIDES.

MANGANOUS, MnO

Preparation.—Ignition of $MnCO_3$ in hydrogen gas.

MANGANIC, Mn_2O_3.—Found native.

Preparation.—By heating MnO.

PEROXIDE, MnO_2.—Found native.

MANGANOUS MANGANIC, Mn_3O_4

Preparation.—*θ.* $3MnO_2 = Mn_3O_4 + O_2$

CHLORIDES.

MANGANOUS CHLORIDE, $MnCl_2$

Preparation.—Bye product in the manufacture of chlorine from MnO_2 and HCl

MANGANIC CHLORIDE, Mn_2Cl_6.—Unstable, and decomposed by heat.

Preparation.—By dissolving Mn_2O_3 in cold HCl

Another chloride having the formula $MnCl_7$ is supposed to exist.

SULPHATE, $MnSO_4$

Preparation.—$MnO_2 + C = MnO + CO$

$MnO + H_2SO_4 = MnSO_4 + H_2O$

Used in dyeing.

MANGANIC ANHYDRIDE, MnO_3.—Not known in the free state, but combined to form manganates (*all coloured green*).

Preparation of *manganate of potassium* (K_2MnO_4):

θ. $MnO_2 + K_2CO_3 = K_2MnO_4 + CO$

Preparation of permanganate of potassium, $KMnO_4$:

θ. $3KMnO_4 + 2H_2O = 2KMnO_4 + 4KHO + \sqrt{MnO_2}$

Salts are purple coloured.

If $KMnO_4$ be distilled with strong sulphuric acid, a greenish black liquid distils over, which is permanganic acid.

θ. $2KMnO_4 + H_2SO_4 = K_2SO_4 + H_2O + Mn_2O_7$

Chromium.—Cr = 52·5.

Occurrence.—Chrome iron ore, $FeO.Cr_2O_3$, and rarely as $PbCrO_4$

Preparation.—By strong ignition of Cr_2O_3 with carbon in a crucible of lime.

Oxides.

Chromous, CrO.—Unstable brown powder.

Preparation.—$2KHO + CrCl_2 = \sqrt{CrO,H_2O,} + 2KCl$.

Chromic, Cr_2O_3.—Green powder.

Preparation.—

θ. $2(K_2CrO_4CrO_3) = 2K_2CrO_4 + O_3 + Cr_2O_3$

Chromous Chromic, Cr_3O_4

Preparation.—By exposing hydrated CrO to air.

Chromic Anhydride, CrO_3.—Red deliquescent crystals.

Preparation.—In aqueous solution—

$K_2CrO_4CrO_3 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3$

Reactions.—

(Solid) $2CrO_3 + 12HCl = Cr_2Cl_6 + 3Cl_2 + 6H_2O$

(Aqueous) $2CrO_3 + 3SO_2 = Cr_23SO_4$

PREPARATION OF CHROMATES OF POTASSIUM.

NORMAL CHROMATE.—Chrome iron ore is roasted in air with carbonate of potash.

BICHROMATE OR ANHYDRO CHROMATE, $K_2CrO_4CrO_3$

$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2CrO_4CrO_3 + H_2O$

CHLORIDES.

Chromous, $CrCl_2$.—White substance, unstable, and soluble in H_2O to a blue liquid. Prepared as above.

SULPHATE, Cr_23SO_4

Preparation.—By solution of hydrated chromic oxide in dilute sulphuric acid.

Nickel Sub-Group.—Ni, Co, and Ur.

General characters.—They have two oxides, both basic, but the highest one is very feeble. The principal salts are those of the *ous* oxide. The salts are all coloured.

Cobalt.—Co = 59.

Occurrence.—As arsenide, $COAs_2$ (*tin white cobalt*); also as arsenide and sulphide, $CoAs_2CoS_2$ (*cobalt glance*).

Preparation.—θ. $\underset{\text{Oxalate.}}{CoC_2O_4} = Co + 2CO_2$

Properties.—Reddish hard metal.

Oxides.

Cobaltous, CoO.—Black powder.

Preparation.—By action of heat on carbonate. Forms salts which are red in the hydrated condition and green in the anhydrous state.

Cobaltic, Co_2O_3, very unstable.

Preparation.—$2CoO + H_2O + Cl_2 = \sqrt{Co_2O_3} + 2HCl$

Cobaltous Cobaltic, Co_3O_4

Preparation.—(*a.*) By action of heat on CoO in air.

(*b.*) θ. $Co2NO_3 = Co_3O_4 + 3N_2O_4 + O_2$

Nickel.—Ni = 58·8.

Occurrence.—As kupfernickel, $NiAs_2$

Preparation.—Similar to cobalt.

Properties.—Hard white lustrous metal. Soluble in HCl and H_2SO_4 slowly, but with ease in HNO_3; nickelous salts being formed in each case.

Oxides.

Nickelous, NiO.—Grey powder.

Preparation.—Action of heat in the nitrate. Forms salts, which are green in the hydrated and yellow in the anhydrous condition.

NICKELIC, Ni_2O_3

Preparation. — By passing chlorine through cold nickelous hydrate. It is very unstable. It is dissolved in HCl with evolution of chlorine, forming nickelous chloride.

CHLORIDES.

NICKELOUS, $NiCl_2$

Powder prepared by action of Cl on the metal or by dissolving oxide in HCl.

SULPHATE.

$NiSO_4$.—Most important salt.

Preparation.—By dissolving the oxide in H_2SO_4

Copper Group.

Cu, Hg, Ag, Pb.

Silver.—Ag = 108, a Monad.

Occurrence. — Native in small quantities, chiefly as sulphide mixed with galena or sulphide of lead; also as chloride.

Preparation.—The ore is crushed and roasted with common salt, by which the metal is converted into chloride. The mass is now agitated with water and scrap iron, when the silver is separated

in the metallic condition. Mercury is next added, which forms an amalgam with the silver. On distillation the mercury is volatilised and the silver left.

Separation of Ag from Galena.
(Pattinson's Process.)

The lead containing the silver is melted and slowly cooled, when the lead crystallises first, and is removed. This process is repeated several times, until an alloy rich in silver is obtained, which is then submitted to *cupellation* as follows:—The alloy is melted in a shallow tray, lined with bone ash, and subjected to a blast of air, which oxidizes the lead to PbO, which is absorbed by the porous bone ash, leaving the silver almost in a pure condition.

Properties.—White lustrous metal.

Oxides.

Only one basic oxide, Ag_2O.—A brown powder.

Preparation.—

$$2AgNO_3 + 2KHO = \sqrt{Ag_2O} + 2KNO_3 + H_2O$$

Reactions.—Decomposed by heat into metal and oxygen; hence silver is a noble metal.

Chlorides.

There are two, AgCl and Ag_2Cl, or subchloride.

AgCl.—White powder, insoluble in H_2O, but soluble in ammonia.

Preparation.—$AgNO_3 + HCl = \sqrt{AgCl} + HNO_3$

It is turned violet by the action of light, being converted into subchloride, Ag_2Cl

Nitrate.

$AgNO_3$.—Colourless tabular crystals; or if fused, in white sticks, easily soluble in water.

Preparation.—

$3Ag_2 + 8HNO_3 = 6AgNO_3 + N_2O_2 + 4H_2O$

Alloys.—Silver coinage contains 7·5 per cent. of Cu

Lead.—Pb = 207, a Dyad.

Occurrence.—As sulphide PbS. (galena), as sulphate $PbSO_4$ (anglesite), and carbonate $PbCO_3$

Preparation.—Ore is roasted in air, when a portion becomes oxidized to $PbSO_4$ and a part reduced to oxide. The following reactions then occur:—

$$\begin{cases} \theta.\ 2PbO + PbS = Pb_3 + SO_2 \\ \theta.\ PbSO_4 + PbS = Pb_2 + 2SO_2 \end{cases}$$

Properties.—Bluish white metal, very soft, and when melted in contact with air converted to oxide—PbO

Oxides.

Litharge, PbO.—Yellow powder or in brown scales. Soluble in KHO. Forms salts.

Preparation.—By heating lead in air.

MINIUM (*Red Lead*), $2PbO.PbO_2$.—Red powder.

Preparation.—By heating litharge in air.

Reactions.—At a high temperature it is decomposed with PbO and O.

Action of HNO_3 *on Red Lead.*

$$2PbO.PbO_2 + 2HNO_3 = 2(Pb2NO_3) + \sqrt{PbO_2} + H_2O$$

PUCE, PbO_2 (*Peroxide of Lead*).—A brown powder.

Preparation.—As above.

Reactions.—Not soluble in dilute acids. Decomposed by HCl

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

Soluble in potassic or sodic hydrates.

$$PbO_2 + 2KHO = K_2PbO_3 + H_2O$$

CHLORIDE.

$PbCl_2$.—White powder. Insoluble in cold water, but soluble in boiling water, from which it separates out on cooling.

Preparation.—By precipitation.

SULPHIDE.

PbS.—Found native, also by precipitation. Black, lustrous, laminated mass as galena; black powder, if made by precipitation.

Reactions.—(*a.*) Nitric acid converts it to sulphate.

(*b.*) $PbS + 2HCl = PbCl_2 + H_2S$

Iodide.

PbI_2.—Yellow powder or crystals.

Preparation.—$Pb2NO_3 + 2KI = \sqrt{PbI_2} + 2KNO_3$
In aqueous solution.

Carbonate.

$PbCO_3$.—White lead. White insoluble powder.

Preparation.—(*a.*) By exposing lead to the vapour of acetic acid and CO_2, the latter derived from spent tan. Usually contains hydrate when made in this way ($2PbCO_3.Pb2HO$).

(*b.*) $3PbO + 2HC_2H_3O_2 = Pb2C_2H_3O_2.2Pb2HO$
Basic acetate.

$Pb2C_2H_3O_2.2Pb2HO + 2CO_2 = \sqrt{2PbCO_3} + Pb2C_2H_3O_2 + H_2O$

Acetate.

(*Sugar of Lead.*) $Pb2C_2H_3O_2$.—White crystals, soluble in water.

Prepared as above.

Chromate.

$PbCrO_4$ (*Chrome Yellow*).

Preparation.—$Pb2NO_3 + K_2CrO_4 = \sqrt{PbCrO_4} + 2KNO_3$

Alloys.—

Lead and	Tin,	= Solder and Pewter.
,,	Arsenic,	= Shot metal.
,,	Tin and Antimony,	= Type metal.

Mercury.—Hg = 200, Dyad.

Occurrence.—Native, and as sulphide (cinnabar).

Preparation.—*θ.* $4HgS + 4CaO = CaSO_4 + 3CaS + 4Hg$

Properties.—Lustrous, heavy, volatile liquid, uniting with other metals to form amalgams. Combines at ordinary temperature with Cl, Br, I.

Oxides.

Mercurous, Hg_2O.—Black unstable powder.

Prep.—$Hg_2Cl_2 + 2KHO = 2KCl + H_2O + \sqrt{Hg_2O}$

Mercuric, HgO.—(*a.*) Red (*crystalline*); (*b.*) Yellow (*amorphous*).

Preparation.—(*a.*) *θ.* $Hg2NO_2 = HgO + N_2O_4 + O$

(*b.*) $HgCl_2 + 2KHO = \sqrt{HgO} + H_2O + 2KCl$

Chlorides.

Mercurous, Hg_2Cl_2 (*Calomel*).—Heavy, white, insoluble powder.

Preparation.—*θ.* $Hg_2SO_4 + NaCl = Hg_2Cl_2 + Na_2SO_4$

Mercuric, $HgCl_2$ (*Corrosive Sublimate*).—White soluble crystals.

Preparation.—*θ.* $HgSO_4 + 2NaCl = HgCl + Na_2SO_4$

Iodide.

Mercurous, Hg_2I_2.—Green powder, unstable. Prepared by direct union.

MERCURIC, HgI_2.—Red powder.

(*In aqueous solution*) $2KI + HgCl_2 = \sqrt{HgI_2} + 2KCl$

SULPHATES.

MERCUROUS, Hg_2SO_4.—Prepared by subliming mercuric sulphate and mercury together.

MERCURIC, $HgSO_4$.—Grey powder.

Preparation.—*θ.* $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$

NITRATES.

MERCUROUS, $HgNO_3$.—White crystals, decomposed by excess of water.

Preparation.—By dissolving mercury in cold dilute nitric acid.

MERCURIC, $Hg2NO_3$.—White crystals.

Preparation.—By dissolving mercury in concentrated hot nitric acid.

SULPHIDES.

MERCURIC, HgS.—Allotropic. Black if made by precipitation, red if sublimed.

AMMONIO CHLORIDES.

WHITE PRECIPITATE.

Preparation.—$HgCl_2 + 2NH_4HO + \sqrt{NH_2HgCl} + NH_4Cl + 2H_2O$

BLACK PRECIPITATE.

$$Hg_2Cl_2 + 2NH_4HO = \sqrt{NH_2Hg_2Cl} + NH_4Cl + 2H_2O$$

The following formulæ will show their relation :—

Ammonic chloride.	White precipitate.	Black precipitate.
$N\left\{\begin{matrix}H'_2\\H'_2\\Cl'\end{matrix}\right.$	$N\left\{\begin{matrix}H'_2\\Hg''\\Cl'\end{matrix}\right.$	$N\left\{\begin{matrix}H'_2\\Hg'_2\\Cl'\end{matrix}\right.$

Copper.—Cu = 63·5, Dyad.

Occurrence.—Native; also as carbonate and sulphide.

Preparation.—Ore roasted in current of air. The sulphide of iron is converted to oxide, the sulphide of copper remaining unchanged. It is now heated with sand, which removes the iron as silicate. The residue is strongly heated in a current of air, and the molten mass stirred with a pole of green wood, when the sulphide of copper is reduced to oxide, which is further reduced to metal by means of the undecomposed sulphide and by the carbon of the wood.

Properties.—Malleable ductile metal with a characteristic colour; unaltered in dry air at ordinary temperature, but if heated is converted into CuO. Dilute H_2SO_4 or HCl have no action on it.

OXIDES.

CUPROUS, Cu_2O.—Red powder.

Preparation.—*θ.* $CuO + Cu = Cu_2O$

It dissolves in oxygen acids to form cupric salts.

CUPRIC OXIDE, CuO.—Black powder.

Preparation.—*θ.* $Cu2NO_3 = CuO + N_2O_4 + O$

In the hydrated condition it is blue.

$$Cu2NO_3 + 2KHO = \sqrt{Cu2HO} + 2KNO_3$$

CHLORIDES.

CUPROUS, Cu_2Cl_2.—White insoluble powder.

Preparation.—*θ.* $Cu + CuO + 2HCl = Cu_2Cl_2 + H_2O$

It is soluble in NH_4Cl to a colourless liquid, but it rapidly absorbs oxygen and turns blue, becoming converted to $CuCl_2$

CUPRIC, $CuCl_2$.—Green crystals.

Preparation.—$CuO + 2HCl = CuCl_2 + H_2O$

SULPHATE.

$CuSO_4$.—(*Blue stone—Blue vitriol.*)

Preparation.—*θ.* $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$

AMMONIO SULPHATE.

$Cu\ (NH_4)_2\ (NH_2)_2\ SO_4$.—Blue crystals.

Preparation.—By adding ammonia to aqueous sulphate of copper until precipitate at first formed is nearly redissolved, and precipitating the salt by alcohol.

The following formula will show its construction:

$$N_2\left\{\begin{matrix}H_2\\H_2\\H_2\\H_2\end{matrix}\right\}SO_4 \qquad N_2\left\{\begin{matrix}Cu\\(NH_4)_2\\H_2\\H_2\end{matrix}\right\}SO_4$$

Ammonic sulphate. Ammonic cupric sulphate.

ALLOYS OF COPPER.—

Brass, Cu and Zn.

Bell Metal and Gun Metal, Cu and Sn.

Bronze, Cu, Sn, Zn, and Pb.

Copper Coinage, 95 per cent. of Cu.
4 „ Sn.
1 „ Zn.

Platinum Group.

Au, Pt, and Pd.

General Characters.—They do not unite directly with oxygen. Their oxides are decomposed by heat alone. They are soluble only in aqua regia, and are usually found native.

Gold.—Au = 197, Triad.

Occurrence.—Free in quartz.

Preparation.—By washing away the quartz and amalgamating with mercury. On distilling the mercury the gold is left.

Properties.—Yellow soft metal. Most malleable and ductile of all the metals.

Reactions.—Its salts are precipitated from aqueous solutions by ferrous sulphate, oxalic acid, and trichloride of antimony.

$$\theta.\begin{cases} 2AuCl_3 + 6FeSO_4 = 2(Fe_2 3SO_4) + Fe_2Cl_6 + \sqrt{Au_2} \\ 2AuCl_3 + 3H_2C_2O_4 = 6CO_2 + 6HCl + \sqrt{Au_2} \\ 3SbCl_3 + 2AuCl_3 = 3SbCl_5 + \sqrt{Au_2} \end{cases}$$

Oxides.

Two; one basic, Au_2O, one acid, Au_2O_3

Aurous, Au_2O

Preparation.—By adding KHO to aqueous aurous chloride.

Chlorides.

Aurous, AuCl.—Unimportant.

Auric, $AuCl_3$.—Prepared by dissolving gold in nitro-hydrochloric acid. It forms double salts with the alkaline metals.

Alloys.—Jeweller's gold contains in every 24 parts 18, 15, 12, or 9 parts of gold, called carats, the remaining portion consisting of copper. Gold coinage contains one part of copper in eleven parts of gold.

Platinum.—Pt = 197, Tetrad.

Occurrence.—Found native with Palladium, Iridium, and other rare metals.

Preparation.—The ore is dissolved in aqua regia, and the platinum separated from the other metals by precipitation.

OXIDES.—Two, PtO and PtO_2

The chief salt is the chloride, which is made by dissolving the metal in aqua regia. Like gold chloride, it forms double salts with the alkaline metals.

Antimony Group.

As, Sb, Bi, and Sn.

General Characters.—They all partake of the nature both of metals and non-metals; hence the group is sometimes termed *bastard metals.* Arsenic and antimony unite with hydrogen to form compounds analogous to ammonia (NH_3). On heating in air they are all converted into oxides; bismuth with difficulty, the others with ease. They are all spontaneously inflammable in chlorine, forming volatile chlorides, all of which, with the exception of tin, are decomposed by water, with the formation of oxychlorides.

Arsenic.—As = 75, Triad.

Occurrence.—Combined with sulphur and various metals.

Preparation.—Ore roasted and converted to As_2O_3

$$\theta.\ As_2O_3 + 3C = As_2 + 3CO$$

Properties.—Steel grey crystalline mass; burning with white flame to As_2O_3

OXIDES.

ARSENIOUS, As_2O_3 (*White Arsenic*).—White translucent masses, resembling broken china, or in octahedral crystals.

Preparation.—By roasting arsenical ores in air.

Properties.—Unites with bases to form arsenites, which are unstable, and not well defined. It unites with water to form a hypothetical arsenious acid, H_3AsO_3. It corresponds to phosphorous acid in many respects.

ARSENIC, As_2O_5.—White amorphous mass.

Preparation.—

(*a.*) $\theta.$ $\begin{cases} As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3 \\ \theta. \quad 2H_3AsO_4 = As_2O_5 + 3H_2O \end{cases}$

(*b.*) $As_2O_3 + 5H_2O + 2Cl_2 = 2H_3AsO_4 + 4HCl$

Reactions.—Decomposed by strong heat.

$$\theta. \quad As_2O_5 = As_2O_3 + O_2$$

The hydrated acid corresponds to phosphoric acid.

CHLORIDE.

$AsCl_3$.—Colourless volatile liquid.

Preparation.—(*a.*) $\theta.$ $As + Cl_3 = AsCl_3$

(*b.*) $\theta.$ $As + 6HgCl_2 = 3Hg_2Cl_2 + 2AsCl_3$

Reactions.—Decomposed by water:

$$2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$$

HYDRIDE.

AsH_3 (*Arsenuretted Hydrogen*).—A gas.

Preparation.—By adding any compound of arsenic to an apparatus evolving hydrogen.

$$H_3AsO_3 + 3H_2 = AsH_3 + 3H_2O$$

Properties.—Colourless poisonous gas, burning in air to As_2O_3 and H_2O:

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O$$

With limited supply of air:

$$4AsH_3 + 3O_2 = As_4 + 6H_2O$$

The above reaction takes place when a cold surface is depressed into the flame, and the deposit so formed is soluble in aqueous solution of bleaching powder.

If passed into aqueous solutions of the following substances, the several reactions take place.

$$6AgNO_3 + 3H_2O + AsH_3 = \overline{\sqrt{3Ag_2}} + 6HNO_3 + H_3AsO_3$$

$$6CuSO_4 + 4AsH_3 = \overline{\sqrt{2(Cu_3As_2)}} + 6H_2SO_4$$

If passed over heated $HgCl_2$:

$$\theta.\ 6HgCl_2 + 2AsH_3 = 3Hg_2Cl_2 + 6HCl + As_2$$

It is dissociated by heat.

The production of this gas and its subsequent decompositions, as shown above, are used in testing under the name of *Marsh's process.*

Sulphides.

Realgar, As_2S_2.—Red solid, found native.

Preparation.—By fusing As and S together.

Reaction.—Soluble in alkaline hydrates. If heated in air:

$$\theta.\ As_2S_2 = As_2O_5 + S_2$$

ORPIMENT, As_2S_3.—Yellow powder, found native.

Preparation.—$As_2O_3 + 3H_2S = \sqrt{As_2S_3} + 3H_2O$ (aqueous).

N.B.—If H_2S be added to aqueous As_2O_3, the oxide is first reduced and then a precipitate of As_2S_3 falls down.

$$As_2O_3 + 2H_2S = \sqrt{S_2} + As_2O_3 + 2H_2O$$

Reactions.—Soluble in alkaline hydrates like As_2S_2:

$$As_2S_3 + 4KHO = \underset{\text{Arsenite of potassium.}}{K_2HAsO_3} + \underset{\text{Sulpharsenite of potassium.}}{K_2HAsS_3}$$

Hence it is argued that the sulphides of arsenic are sulphur acids.

Antimony.—Sb = 122, Triad.

Occurrence.—Native, but chiefly as sulphide.

Preparation.—*θ.* $Sb_2S_3 + 3Fe = 3FeS + Sb_2$

Properties.—Greyish brittle metal with brilliant lustre.

OXIDES.

ANTIMONOUS, Sb_2O_3.—White powder, found native.

Preparation.—*θ.* $2Sb + 3O = Sb_2O_3$
If heated in air it forms Sb_2O_4

ANTIMONIC, Sb_2O_5.—Yellow powder.

Preparation.—

θ. $2Sb + 4HNO_3 = Sb_2O_5 + N_2O_3 + N_2O_2 + 2H_2O$

This acid unites with water to form two distinct acids:

$HSbO_3$, Antimonic acid.
$H_4Sb_2O_7$, Metantimonic acid.

(See also page 53—*Action of* Na_2CO_3 *on Chlorides of Antimony.*)

TABLE XXVIII.

Comparison of Phosphoric and Antimonic Acids.

Orthophosphoric Acid, H_3PO_4	Orthoantimonic Acid? H_3SbO_4, not known.
	Orthoantimoniate of Antimony, Sb,SbO_4, known.
Metaphosphoric Acid, HPO_3	Antimonic Acid, $HSbO_3$
Pyrophosphoric Acid, $H_4P_2O_7$	Metantimonic Acid, $H_4Sb_2O_7$

Chlorides.

Antimonous, $SbCl_3$ (*Butter of Antimony*).—White buttery mass.

Preparation.—θ. (*a.*) $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$

Properties.—Soft buttery mass, or in deliquescent crystals, soluble in HCl. Powerful corrosive.

The commercial preparation is usually coloured yellow, from presence of iron. It is decomposed by water:

$$SbCl_3 + H_2O = \sqrt{SbOCl} + 2HCl$$

SbOCl is a white powder, which gradually becomes crystalline, and of a brownish yellow colour (*powder of algaroth*).

ANTIMONIC, $SbCl_5$.—Colourless liquid.

Preparation.—By passing excess of chlorine over metallic antimony gently heated.

Reactions.—$2SbCl_5 + 7H_2O = \overline{4H_4Sb_2O_7} + 10HCl$

HYDRIDE.

SbH_3.—A gas.

Preparation.—By adding any compound of antimony to an apparatus evolving hydrogen.

Properties.—Colourless poisonous gas, burning in air with a greenish flame to Sb_2O_3 and water.

$$\theta.\ 2SbH_3 + 3O_2 = Sb_2O_3 + 3H_2O$$

If the supply of air is small, then

$$4SbH_3 + 3O_2 = Sb_4 + 6H_2O$$

Hence a cold surface depressed in the flame produces a purple-coloured stain, which is insoluble in solution of bleaching powder, but soluble in ammonic sulphide.

If passed into aqueous nitrate of silver:

$$^*\ SbH_3 + 3AgNO_3 = \overline{SbAg_3} + 3HNO_3$$

It dissociates if passed through a red-hot tube.

The production of this gas and its subsequent decompositions, as shown above, are used in testing under the name of *Marsh's process.*

* Compare this with the corresponding reaction with AsH_3

Sulphides.

Antimonous, Sb_2S_3.—(*Native*), Steel grey mass; (*artificial*), orange red powder.

Preparation.—$2SbCl_3 + 3H_2S = \sqrt{Sb_2S_3} + 6HCl$

Properties.—Orange powder soluble in alkaline sulphides; if heated in air, is converted to golden sulphide, Sb_2OS_2

$$\theta.\ Sb_2S_3 + 3O_2 = Sb_2OS_2 + SO_2$$

Antimonic, Sb_2S_5.—Deep orange powder.

Preparation.—$2SbCl_5 + 5H_2S = \sqrt{Sb_2S_5} + 10HCl$

Tartar Emetic.

$KSbOC_4H_4O_6$.—White octahedral crystals.

Preparation.—

$$\theta.\ Sb_2O_3 + 2KHC_4H_4O_6 = 2KSbOC_4H_4O_6 + H_2O$$

Acid tartrate of potash in aqueous solution.

The following will show the constitution of the salt:

$KKC_4H_4O_6$ = Normal tartrate of potassium.
$KHC_4H_4O_6$ = Acid „ „
$KSbOC_4H_4O_6$ = Tartar emetic.

It is the only compound of antimony which is freely soluble in water.

TABLE XXIX.

Reasons for classing Arsenic and Antimony amongst the Non-Metals.

NH_3	PH_3	AsH_3	SbH_3	Hydrides.
NCl_3	PCl_3	$AsCl_3$	$SbCl_3$	Chlorides.
—	PCl_5	—	$SbCl_5$	
N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Oxides.
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	
—	H_3PO_3	H_3AsO_3	H_3SbO_3	Acids.
—	H_3PO_4	H_3AsO_4	—	
—	$H_4P_2O_7$	$H_4As_2O_7$	$H_4Sb_2O_7$	
HNO_3	HPO_3	$HAsO_3$	$HSbO_3$	

Bismuth.—Bi = 210, Triad.

Occurrence.—Native in quartz.

Preparation.—Smelted out from the quartz.

Properties.—Silvery white metal with yellow lustre; volatile and combustible in air to Bi_2O_3

Oxides.

Three, BiO, Bi_2O_3, Bi_2O_5

Monoxide, BiO, is an unstable body and non-basic.

Bismuthous, Bi_2O_3.—Pale yellow powder.

Preparation.—Ignition of $BiONO_3$ (*basic nitrate*). This is really the only basic oxide.

Bismuthic, Bi_2O_5.—Reddish powder, acts usually as an acid oxide.

Preparation.—By passing chlorine into Bi_2O_3 suspended in KHO solution.

Chloride.

$BiCl_3$.—White powder; volatile and deliquescent.

Preparation.—By direct union of Bi and Cl.

Reactions.—$BiCl_3 + H_2O = \underset{\text{Oxychloride.}}{\sqrt{BiOCl}} + 2HCl$.

Nitrate.

$Bi3NO_3$.—Colourless crystals.

Preparation.—By dissolving the oxide Bi_2O_3 in HNO_3

Reactions.—Decomposed by water:

$$4Bi3NO_3 + 4H_2O = 4(BiONO_3) + 8HNO_3$$

Alloys.—Fusible metal, consists of Bi, Pb, and Sn.

Tin.—Sn = 118, Dyad and Tetrad.

Occurrence.—Chiefly as SnO_2 (tin-stone).

Preparation.—The ore is roasted to free it from arsenic, and then reduced with coal.

$$\theta.\ SnO_2 + 2C = Sn + 2CO$$

Properties.—Silvery white crystalline metal; soluble in HCl and in alkaline hydrates.

$$\theta.\ 2NaHO + Sn = \underset{\text{Sodic stannate.}}{Na_2SnO_3} + 2H_2$$

Oxides.

Two, both basic.

Stannous, SnO.—Black powder.

Preparation.—Ignition of hydrate $2SnO.H_2O$ in a current of CO_2

The hydrate is precipitated from $SnCl_2$ by KHO

STANNIC, SnO_2.—Native (*black*); artificial (*yellowish white powder*).

Preparation.—

(*a.*) By passing steam over red-hot stannic chloride:

θ. $SnCl_4 + 2H_2O = SnO_2 + 4HCl$

(*b.*) θ. $Sn + 4HNO_3 = SnO_2 + 2N_2O_4 + 2H_2O$

(*c.*) θ. $Sn + O_2 = SnO_2$

Stannic oxide forms two hydrates with water:

H_2SnO_3— Stannic acid $= SnO_2.H_2O$

$H_2Sn_5O_{11}$—Meta „ „ $= 5SnO_2.H_2O$

The latter goes by the name of *putty powder*.

CHLORIDES.

STANNOUS, $SnCl_2$.—Grey resinous mass (tin salt).

Preparation.—(*a.*) Anhydrous:

θ. $Hg_2Cl_2 + Sn = SnCl_2 + Hg_2$

(*b.*) In solution:

θ. $Sn + 2HCl + SnCl_2 + H_2$

Reactions.—Powerful reducing agent.

Action on aqueous $HgCl_2$

$2HgCl_2 + SnCl_2 = SnCl_4 + \sqrt{Hg_2Cl_2}$

$Hg_2Cl_2 + SnCl_2 = SnCl_4 + \sqrt{Hg_2}$

STANNIC, $SnCl_4$. — (*Anhydrous*) Fuming colourless liquid; (*hydrated*) deliquescent colourless crystals, $SnCl_4 5H_2O$

Preparation.—

θ. (*a.*) $Sn + 2Cl_2 = SnCl_4$

(*b.*) $Sn + 2HgCl_2 = SnCl_4 + Hg_2$
Both methods give the anhydrous salt.

(*c.*) In solution :

(1.) $SnCl_2 + Cl = SnCl_4$

(2.) $SnCl_2 + 2HCl + 2HNO_3 = SnCl_4 + N_2O_2 + 4H_2O$

SULPHIDES.

STANNOUS, SnS.—Brown powder.

Preparation.—$SnCl_2 + H_2S = \sqrt{SnS} + 2HCl$

STANNIC, SnS_2.—Yellow powder.

Preparation.—$SnCl_4 + 2H_2S = \sqrt{SnS_2} + 4HCl$

CHEMICAL PHYSICS OF THE ATMOSPHERE.

The atmosphere is supposed to extend to a height of forty-five miles, the lower portion being condensed by the weight of that above it. As we ascend, the air becomes rarer, until at a height of five miles it will no longer support life.

At the sea level the pressure exerted by this ocean of air is equivalent to a little more than fifteen pounds on each square inch, or in metrical measure, 1·033 kilograms on each square centimetre. The pressure so exerted is equal in all directions.

The Barometer.

The barometer is an instrument to measure the pressure of the atmosphere. It consists of a tube about 33 inches or 800 mm. long, and closed at one end. It is filled with mercury, and immersed at the open end into a cistern containing the same metal. Under normal conditions the mercury will then sink in the tube to 30 inches, or 760 mm.—this being the normal pressure. The space between the mercury and the closed end of the tube is a perfect vacuum, called after the discoverer, Torricelli. If the pressure of the air increases the mercury rises; if the pressure diminishes the mercury falls.

The Air a mixture, not a compound.

There are four reasons for coming to this conclusion, viz. :—

1*stly.* The proportions in which nitrogen and oxygen exist in air (21°/₀ of O and 79°/₀ of N) are not those of the combining weights; hence, if it were a compound the first law of combination would be violated.

2*dly.* When nitrogen and oxygen are mixed in the proportions in which they exist in air no rise in temperature nor alteration of volume takes place. Both these phenomena usually accompany chemical action.

3*dly.* The proportions of oxygen and nitrogen are not constant, slight variations occurring in the composition of air from various localities. If it were a compound, this would be another violation of the first law.

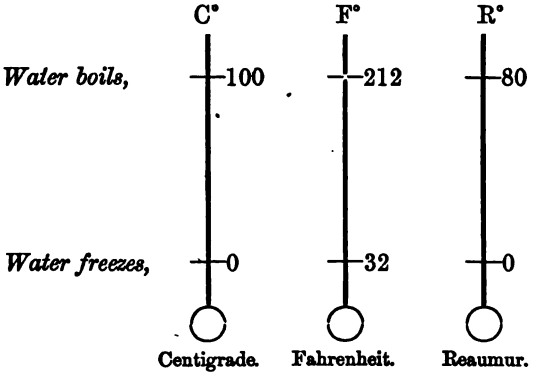
4*thly.* If air be dissolved in recently boiled distilled water, and then expelled, the composition of the expelled air differs from ordinary air, inasmuch as it is richer in oxygen. If it were a compound it would be unaltered in composition.

The Thermometer.

The thermometer is usually a tube closed at both ends, containing either alcohol or mercury, and used to measure the temperature.

The alcoholic is used for low temperature; the mercurial is used for high temperature.

There are three methods of graduation commonly adopted. The following diagram will show the relation between these various forms.



To CONVERT DEGREES OF ONE SCALE INTO THOSE OF ANOTHER.

Centigrade to Fahrenheit.

Multiply by 9, divide product by 5, and add 32; or

$$\frac{\text{C.} \times 9}{5} + 32 = \text{F.}$$

Example.—Convert 60° C. to Fahrenheit degrees.

$$\frac{60 \times 9}{5} = 140° \text{ F.}$$

Fahrenheit to Centigrade.

Subtract 32, multiply product by 5, and divide by 9; or

$$\frac{\text{F.}-32 \times 5}{9} = \text{C.}$$

Example.—Convert 212° F. to Centigrade degrees.

$$212-32 = 180$$
$$\frac{180 \times 5}{9} = 100^{\circ}\ \text{C.}$$

The Reaumur scale is little used, and calculations involving its use seldom find a place in examination papers. The following formulæ will give the results if required.

Fahrenheit to Reaumur, $\frac{\text{F.}-32 \times 4}{9} = \text{R.}$

Reaumur to Fahrenheit, $\frac{\text{R.} \times 9}{4} + 32 = \text{F.}$

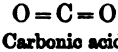
Centigrade to Reaumur, $\frac{\text{C.} \times 4}{5} = \text{R.}$

Reaumur to Centigrade, $\frac{\text{R.} \times 5}{4} = \text{C.}$

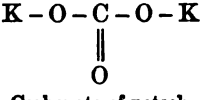
ORGANIC CHEMISTRY.

There is no sharp line of demarcation between Inorganic and Organic Chemistry. The latter is usually described as the chemistry of the carbon compounds. There are, however, carbon compounds which are strictly inorganic. In these the carbon is united to oxygen, whereas in the organic it is united either to carbon, nitrogen, or hydrogen.

Inorganic Carbon Compounds.

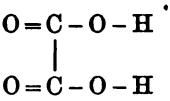


Carbonic acid.



Carbonate of potash.

Organic Carbon Compound.



Oxalic acid.

All organic compounds are changed by heat, and if the heat be applied gradually, new compounds are formed, and the process is called *destructive distillation.*

ORGANIC ANALYSIS.

The substance is burnt in a current of oxygen, and the products passed through a tube containing $CaCl_2$ to absorb H_2O, and through a bulb containing KHO to absorb CO_2; both tube and bulb being weighed at the commencement of the experiment. The increase of weight at the conclusion of the process gives the amount of CO_2 and H_2O respectively, from which the weight of C and H are calculated. The oxygen is estimated by difference. From this analysis is calculated the per-centage composition.

Nitrogen is estimated by combustion of organic substance with soda lime, the nitrogen being evolved as ammonia.

Sulphur and phosphorous are estimated by oxidation with nitric acid, being converted into sulphuric and phosphoric acids respectively.

EMPIRICAL AND RATIONAL FORMULÆ.

Empirical is the per-centage composition divided by the respective atomic weights.

The *Rational* shows how much will combine with, or displace, or play the part of some element of known atomic weight.

Example: *Alcohol.*

C = 52·174 ÷ 12 = 4·348 ÷ 2·174 = 2
H = 13·043 ÷ 1 = 13·043 ÷ 2·174 = 6
O = 34·783 ÷ 16 = 2·174 ÷ 2·174 = 1
100·000

Hence C_2H_6O = *Empirical Formula.*

But there are salts formed from alcohol in which C_2H_5 acts as a base.

Hence C_2H_5HO = *Rational Formula.*

ISOMERISM, &c.

When substances have the same per-centage composition and same empirical formula, but different physical properties, they are said to be *isomeric.*

If they have the same empirical formula, but differ in their reactions, they are *metameric.*

If the empirical formula is the same, but they differ in molecular weight, they are *polymeric.*

HOMOLOGOUS SERIES.

When a series of compounds exist, which differ from each other by CH_2, they are said to be an homologous series. The members of such a series have similar transformations when acted on by the same reagents.

Classification of Organic Compounds.

HYDROCARBONS, with an even number of hydrogen atoms, such as CH_4. They are usually looked upon as hydrides of hydrocarbons, with an uneven number of hydrogen atoms:

e.g., CH_4 is looked on as CH_3H

Marsh gas.	Hydride of methyl.

HALOID ETHERS.—Hydrocarbon radicals combined with either Cl, Br, I, or Fl:

e.g., CH_3Cl (*Methyl chloride*).

NITRO COMPOUNDS.—Hydrocarbon radicals combined with nitryl (NO_2):

e.g., CH_3NO_2 (*Nitro methane*).

AMINES.—Alcoholic radicals combined with amidogen, NH_2. An amine may be described as a molecule of ammonia, in which one, two, or three atoms of hydrogen are replaced by an alcoholic radical.

$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right.$	$N\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$
or	or	or	or
NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Ammonia.	Methylamine.	Di-Methylamine.	Tri-Methylamine.

The amines usually have basic properties.

AMIDES.—Acid radicals united to amidogen.

An amide many be described as a molecule of ammonia in which one or more atoms of hydrogen are replaced by an acid radical. When two atoms are replaced, the compound is sometimes called an imide, when three, a nitrile.

$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.$	$N_2\left\{\begin{matrix}C_2O_2\\H_2\\H\end{matrix}\right.$
or	or	or
NH_3	$C_2H_3ONH_2$	$C_2O_22NH_2$
Ammonia.	Acetamide.	Oxamide.

ALCOHOLS. — Hydrocarbon radicals combined with hydroxyl:

C_2H_5HO C_3H_53HO

OXYGEN ETHERS.—Alcohols in which the hydroxylic hydrogen is replaced by an alcoholic radical or an acid radical.

C_2H_5HO = Ethylic alcohol.
$C_2H_5C_2H_5O$ = ,, oxide.
$C_2H_5(C_2H_3O)O$ = ,, acetate.

SULPHUR ALCOHOLS AND ETHERS.—Alcohols and ethers in which the oxygen is replaced by sulphur. They are usually called mercaptans.

ALDEHYDES.—Compounds intermediate between alcohols and acids. Formed by partial oxidation of alcohols.

C_2H_5HO	C_2H_4O	$C_2H_4O_2$
Alcohol.	Aldehyde.	Acetic acid.

KETONES.—Compounds derived from aldehydes by replacing one atom of hydrogen by an alcoholic radical.

$C_2\{HO, H, H, H$ $C_2\{HO, H, H, CH_3$

Aldehyde. Acetone.

ORGANO-METALLIC COMPOUNDS.—Alcoholic radicals combined with metals.

NaC_2H_5	$Sn4CH_3$
Sodic ethide.	Stannic methide.

ORGANIC ACIDS.—Oxygenated radicals combined with hydroxyl, the hydrogen of which is displaceable.

C_2H_3HO (*Acetic acid*).

ACID HALLIDES.—Oxygenated radicals combined with chlorine, bromine, &c.

C_2H_3OCl (*Acetyl chloride*).

Amylaceous Group.

STARCH, CELLULOSE, AND SUGARS.

STARCH ($C_6H_{10}O_5$), or some multiple.

Occurrence.—In plant life, and probably in some lower forms of animal life.

Properties.—White amorphous powder, having a distinct microscopical structure.

Preparation.—From plants, generally potatoes or rice, by dissolving the cell walls by NaHO.

Reactions.—Turned blue by iodine in the cold. Boiled with dilute mineral acids.

(*a.*) Short time = Dextrin, $C_6H_{10}O_5$

(*b.*) Long time = $C_6H_{10}O_5 + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6}$

If heated in the dry condition it is also converted into dextrin.

CELLULOSE $(C_6H_{10}O_5)_n$.

Occurrence.—In plants, also in linen, cotton, and paper.

Properties.—White, tasteless substance, insoluble in water.

Strong sulphuric acid converts it into a colourless adhesive mass, which, if boiled, is converted into glucose. Unsized paper, if heated with moderately strong sulphuric acid, is converted into vegetable parchment. Acted on by nitric acid, nitro substitution products are formed, in which one, two, or three atoms of hydrogen are replaced by NO_2. Gun cotton is trinitrocellulose.

$$C_6H_{10}O_5 + 3HNO_3 = C_6H_7(3NO_2)O_5 + 3H_2O$$

SUGARS.

There are two groups of sugars:

Sucroses.	Glucoses.
$C_{11}H_{22}O_{11}$	$C_6H_{12}O_6$
Cane.	Dextrose.
Milk.	Levulose.

CANE SUGAR (*Sucrose*).

Occurrence.—Free in sugar cane and beet-root.

Preparation.—Extracted by pressure, and purified by crystallisation.

Reactions.—Decomposed by heat.

$$\theta.\ C_{12}H_{22}O_{11} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulosan.}}{C_6H_{10}O_5}$$

At a higher temperature it is converted into CARAMEL.

Oxidized by HNO_3 to oxalic acid :

$$\theta.\ \begin{cases} C_{12}H_{22}O_{11} + O_6 = 2\underset{\text{Saccharic acid.}}{C_6H_{10}O_8} + H_2O \\ C_6H_{10}O_8 + O_6 = 3C_2H_2O_4 + 2H_2O \end{cases}$$

If boiled with dilute acids it takes up the elements of water, and is converted into dextrose and levulose :

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

It is not directly fermentable.

MILK SUGAR (*Lactose*), $C_{12}H_{22}O_{11}$.—White hard solid.

Occurrence.—In milk.

Preparation.—By evaporating the whey of milk.

Reaction.—If heated with dilute acids converted to GALACTOSE, $C_6H_{12}O_6$

GRAPE SUGAR (*Glucose*), $C_6H_{12}O_6$

Occurrence.—In fruits and animal fluids.

Preparation.—By boiling starch with dilute sulphuric acid, when the starch takes up the elements of water.

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$$

Properties.—White unctuous mass, crystallising with difficulty.

Reactions.—Directly fermentable, producing alcohol, carbonic acid, and minor products. If heated by itself is converted into glucosan, $C_6H_{10}O_5$

There are several isomeric modifications of glucose, distinguished chiefly by their action on polarised light.

Fermentation.

Definition.—Change by aid of a ferment in which bodies of the amylaceous group break up into others of a less complex nature. A ferment is a nitrogenous body in a state of change. There are three principal varieties of true fermentation produced by three distinct fungi respectively:

Vinous, produced by	*Torula.*	Alcohol chief product.	
Acetous, „	„ *Mycoderma.*	Acetic acid	„
*Lactic, „	„ *Bacterium lineola.*	Lactic acid	„

False fermentation is produced by chemical means.

Examples.—

(*a.*) Production of oil of bitter almonds:

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Oil of bitter almonds.}}{C_7H_5HO} + HCN + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

(*b.*) Production of oil of mustard:

$$\underset{\text{Potassic myronate.}}{K_2C_{20}H_{38}S_4N_2O_{19}} = \underset{\text{Oil of mustard.}}{2(C_3H_5CNS)} + 2KHSO_4 + 2C_6H_{12}O_6 + H_2O$$

* Formerly supposed to be caused by pencillium glaucum.

(*c.*) Conversion of tannin into gallic acid :

$$\underset{\text{Tannin.}}{C_{27}H_{22}O_{17}} + 4H_2O = 3\underset{\text{Gallic acid.}}{H_3C_7H_3O_5} + C_6H_{12}O_6$$

Substances like the above which produce glucose, when undergoing decomposition, are called *glucosides.*

ALCOHOLS.

Definition.—A hydrocarbon radical combined with hydroxyl.

There are monatomic, diatomic, and triatomic alcohols, according to the number of molecules of combined HO.

Monatomic.	Diatomic.	Triatomic.
C_2H_5HO	C_2H_42HO	C_3H_53HO
Ethylic alcohol.	Glycol.	Glycerine.

These are in turn divided into primary, secondary, and tertiary alcohols.

All the alcohols are looked upon as derived from CH_3HO, methyl alcohol or carbinol, by replacement of hydrogen atoms in the radical by monad radicals of the (C_nH_{2n+1}) series.

$CHHH(HO)$, Carbinol.
$CHHCH_3(HO)$, Methyl carbinol or ethylic alcohol.
$CHHC_2H_5(HO)$, Ethyl carbinol or propylic alcohol.

If only one atom of H replaced = Primary alcohol.
If two atoms of H replaced = Secondary ,,
If three atoms of H replaced = Tertiary ,,

All the alcohols can be prepared by distilling their haloid salts with an alkaline hydrate :

$$\underset{\text{Ethylic chloride.}}{\theta.\ C_2H_5Cl} + KHO = KCl + \underset{\text{Ethylic alcohol.}}{C_2H_5HO}$$

[redacted]

[redacted]IC ALCOHOL, CH_4O

[redacted]ion.—(a.) From marsh gas.

$$CH_4 + Cl_2 = CH_3Cl + HCl$$
$$\theta. \quad CH_3Cl + KHO = CH_4O + KCl$$

Destructive distillation of wood.—See page 16.

[redacted]ties.—If pure, a colourless mobile **liquid, with** [redacted]asant taste and smell. Ordinary **wood spirit is** [redacted]pure, and is of a yellow colour, **with a strong** [redacted]greeable odour. It is inflammable.

Methylated spirit is ethylic alcohol **containing** [redacted]0 per cent. of CH_4O

It undergoes oxidation, producing **formic acid :**

$$CH_4O + O_2 = HCHO_2 + H_2O$$

[redacted]IC ALCOHOL, C_2H_6O

[redacted]ration.—(a.) By synthesis :

$$C_2 + H_2 = C_2H_2 \text{ (}\textit{Acetylene}\text{).}$$
$$C_2H_2 + H_2 = C_2H_4 \text{ (}\textit{Olefiant gas}\text{).}$$
$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4 \text{ (}\textit{Sulphovinic acid}\text{).}$$
$$C_2H_5HSO_4 + H_2O = C_2H_6O + H_2SO_4$$

(b.) By fermenta[redacted] from starch or sugar, and subsequent di[redacted]tion. If prepared **from starch** (grain), it [redacted] converted into sugar by aid of a substanc[redacted]ase—formed by artificial means during [redacted]ess of malting. The simplest equati[redacted]enting the change of sugar into alcoh[redacted]llows :

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$$

This, however, does not show the formation of succinic acid and glycerine, both of which are formed in appreciable quantities during the fermentation.

Pure (absolute) alcohol cannot be prepared by this process alone. The strongest commercial spirit contains 13°/₀ of water.

To prepare absolute alcohol from this, distil it over calcic chloride and quicklime.

Properties.—Colourless mobile liquid, with pleasant taste and odour, miscible with water in all proportions, with contraction in volume. Inflammable. Has never been frozen. Undergoes oxidation under favourable circumstances as follows:

$$C_2H_5HO + O = \underset{\text{Aldehyde.}}{C_2H_4O} + H_2O$$

$$C_2H_4O + O = \underset{\text{Acetic acid.}}{HC_2H_3O_2}$$

TABLE XXX.

Action of Chlorine, &c. in Alcohol.

$C_2H_6O + Cl_2 = 2HCl + C_2H_4O$ (*Aldelyde*).
$C_2H_6O + 4Cl_2 = 5HCl + C_2HCl_3O$ (*Chloral*).
$C_2H_6O + 2Cl_2 + H_2O = 4HCl + C_2H_4O_2$ (*Acetic acid*).
$C_2H_6O + HCl = H_2O + C_2H_5Cl$ (*Ethylic chloride*).
$4C_2H_6O + 8Ca2ClO = 3Ca2CHO_2 + 5CaCl_2 + 8H_2O + 2CHCl_3$ (*Chloroform*).

Alcohol is decomposed if passed through a red-hot tube.

$$\theta.\ C_2H_5HO = CH_4 + H_2 + CO$$

ETHERS.

Are of two kinds—oxygen ethers and compound ethers.

OXYGEN ETHERS, formed by replacing hydroxylic hydrogen by an alcoholic radical:

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ Ethylic alcohol. $\qquad$ $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$ Ethylic oxide.

If the alcoholic radicals differ, the compound is a mixed ether:

$\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}O$ Ethyl methyl ether. $\qquad$ $\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O$ Ethyl amyl ether.

COMPOUND ETHERS.—Formed by replacing hydroxyl by an acid radical:

C_2H_5OH Ethylic alcohol. $\qquad$ $C_2H_5NO_3$ Ethylic nitrate.

General Reactions of Oxygen Ethers.—If heated with water under pressure they are decomposed, the corresponding alcohols being produced:

$$\theta.\ (C_2H_5)_2O + H_2O = 2(C_2H_5HO)$$

If digested for some time with sulphuric acid, the corresponding alcoholic acid sulphate is produced:

$$\theta.\ \left\{\begin{matrix}(C_2H_5)_2O + H_2SO_4 = C_2H_5HO + C_2H_5HSO_4\\C_2H_5HO + H_2SO_4 = C_2H_5HSO_4 + H_2O\end{matrix}\right\}$$

If distilled with phosphoric chloride, the chloride of the corresponding alcohol is produced along with oxychloride of phosphorous :

$$\theta.\ (C_2H_5)_2O + PCl_5 = 2(C_2H_5Cl) + POCl_3$$

COMMON ETHER $(C_2H_5)_2O$ (*Ethylic oxide*).—Improperly called sulphuric ether.

Preparation.—By the continuous etherification, process in which a continuous stream of alcohol comes in contact with a limited quantity of sulphuric acid at a temperature of about 130° C.

$$\theta.\ \begin{cases} H_2SO_4 + C_2H_5HO = C_2H_5HSO_4 + H_2O \\ C_2H_5HSO_4 + C_2H_5HO = (C_2H_5)_2O + H_2SO_4 \end{cases}$$

Properties. — Colourless volatile liquid, very inflammable, and its vapour, when mixed with air forms an explosive mixture. It is very slightly soluble in water, and water is very slightly soluble in ether. It is miscible in all proportions with alcohol.

ETHYLIC ACETATE, $C_2H_5C_2H_3O_2$.—(*Acetic ether.*)

Preparation.—

$$\theta.\ NaC_2H_3O_2 + C_2H_5HO + H_2SO_4 = C_2H_5C_2H_3O_2 + NaHSO_4 + H_2O$$

Properties.—Colourless liquid, with pleasant odour.

ETHYLIC NITRITE, $C_2H_5NO_2$

Preparation.—

$$\theta.\ C_2H_5HO + HNO_3 + H_2SO_4 + Cu = C_2H_5NO_2 + CuSO_4 + 2H_2O$$

The Cu is used to reduce the HNO_3, and the H_2SO_4 prevents the formation of nitrate. If the Cu were omitted, a portion of the alcohol would be oxidized to aldelyde.

θ. $2C_2H_5HO + HNO_3 = C_2H_4O + C_2H_5NO_2 + 2H_2O$

If the copper be replaced by urea, then ETHYLIC NITRATE is produced ($C_2H_5NO_3$), as the urea decomposes any nitrous acid which may be formed. (See page 128.)

ETHYLIC NITRATE.—Prepared as above.

Reaction.—

$$C_2H_5NO_3 + \underset{\text{Nascent hydrogen.}}{3H_2} = C_2H_5HO + \underset{\text{Hydroxylamine.}}{NH_2HO} + H_2O$$

ETHYLIC IODIDE, C_2H_5I.—Colourless liquid, unstable, becoming brown from free iodine.

Preparation.—

$$\theta.\ 12(C_2H_5HO) + P_2 + 5I_2 = 10C_2H_5I + \underset{\text{Phosphovinic acid.}}{2(H_2C_2H_5PO_4)} + 4H_2O$$

ETHYLIC SULPHATE $(C_2H_5)_2SO_4$

Preparation.—$(C_2H_5)_2O + SO_3 = (C_2H_5)_2SO_4$

ETHYLIC SULPHIDE $(C_2H_5)_2S$.—Oily liquid.

Preparation.—θ. $2C_2H_5Cl + K_2S = 2KCl + (C_2H_5)_2S$

ETHYLIC HYDROSULPHIDE, C_2H_5HS. — Liquid with strong smell of onions.

Preparation.—

θ. $KC_2H_5SO_4 + KHS = C_2H_5HS + K_2SO_4$
Potassic sulphovinate.

METHYL ETHERS are prepared in a similar manner to the ethyl compounds. The oxide, $(CH_3)_2O$, is a gas. The iodide, chloride, and bromide can be prepared by direct action of the respective acids on the alcohol. The chloride is a gas, the others are liquids.

ALDEHYDES AND THEIR PRODUCTS.

ACETIC, C_2H_4O.—A liquid with pungent smell. Unstable, and easily oxidized to acetic acid.

Preparation.—(*a.*) By oxidation of alcohol:

$$C_2H_5HO + O = C_2H_4O + H_2O$$

(*b.*) By action of Cl on weak alcohol—see page 107.

(*c.*) θ. $KC_2H_3O_2 + KCHO_2 = C_2H_4O + K_2CO_3$

Reactions.—Reduced by nascent hydrogen to alcohol:

$$C_2H_4O + H_2 = C_2H_5HO$$

Unites with ammonia to form a solid crystalline body—aldehyd-ammonia:

$$C_2H_4ONH_3$$

It is converted to chloral by chlorine:

$$C_2H_4O + 3Cl_2 = C_2HCl_3O + 3HCl$$

or

$$2C_2H_4O + 2Cl_2 = \underset{\text{Croton chloral.}}{C_4H_5Cl_3O} + HCl + H_2O$$

This latter, however, is supposed to be derived from butane, C_4H_{10}, and is hence called butyl chloral:

$$C_4H_5\ Cl_3'O''$$

CHLORAL HYDRATE.

Preparation.—By passing a rapid stream of chlorine through absolute alcohol, and gradually increasing the temperature:

$$C_2H_5HO + 4Cl_2 = 5HCl + C_2HCl_3O$$

Chloral is an oily liquid which, in contact with water, forms a white solid crystalline hydrate, smelling strongly of water melons.

Both chloral and its hydrate are decomposed by alkaline hydrates.

$$C_2HCl_3O + KHO = \underset{\text{Potassic formiate.}}{KCHO_2} + \underset{\text{Chloroform.}}{CHCl_3}$$

CHLOROFORM, $CHCl_3$ (*Methenyl chloride*).—Colourless liquid; slightly soluble in water.

Preparation.—By distilling alcohol with slaked lime and bleaching powder, the simplest equation representing the action is shown in Table XXX.; but there are good reasons for supposing the following reactions take place:

$$\theta.\ \left\{\begin{array}{rl} 2C_2H_5HO + O_2 & = 2C_2H_4O + 2H_2O \\ C_2H_4O + 3Cl_2 & = C_2HCl_3O + 3HCl \\ 2C_2HCl_3O + Ca2HO & = Ca2CHO_2 + 2CHCl_3 \end{array}\right\}$$

Alcoholic Acids.

FORMIC—ACETIC—LACTIC.

FORMIC, $HCHO_2$

Occurrence.—Free in ants, stinging nettles, &c.

Preparation.—(*a.*) Oxidation of methylic alcohol:

$$CH_3HO + O = HCHO_2 + H_2O$$

(*b.*) By distilling glycerine and oxalic acid:

$$\theta.\begin{cases} H_2C_2O_4 = HCHO_2 + H_2O \\ C_3H_5 3HO + HCHO_2 = C_3H_5 2HO.CHO_2 \quad (\textit{Monoformin.}) \\ C_3H_5 2HOCHO_2 + H_2O = C_3H_5 3HO + HCHO_2 \end{cases}$$

Properties.—Colourless liquid with pungent odour and strongly acid.

Reactions.—

$$\theta.\ HCHO_2 = CO + H_2O$$

(Either alone or with strong sulphuric acid.)

$$HCHO_2 + Cl_2 = 2HCl + CO_2$$

$$\theta.\ HCHO_2 + HgO = CO_2 + Hg + H_2O$$

All the formiates are soluble. Lead formiate is least so. If heated with strong bases they are converted to oxalates.

$$\theta.\ 2HCHO_2 + BaO = BaC_2O_4 + H_2 + H_2O$$

Ammonium formiate if strongly heated.

$$\theta.\ NH_4CHO_2 = HCN + 2H_2O$$

ACETIC, $HC_2H_3O_2$.—Colourless acid, liquid, with pungent odour. The strongest acid (*glacial*) is solid at ordinary temperature.

Preparation.—(*a.*) By acetic fermentation in the preparation of vinegar, which contains from 5 to 15 %. Vinegar is prepared by allowing weak alcohol to trickle over wood shavings or wood charcoal exposed to air.

(*b.*) By distilling acetate of sodium with sulphuric acid.

θ. $2NaC_2H_3O_2 + H_2SO_4 = Na_2SO_4 + 2HC_2H_3O_2$

Reactions.—Forms chlorine compounds by direct action in which H is displaced atom by atom.

$C_2H_3ClO_2$, Mono chloracetic acid.
$C_2H_2Cl_2O_2$, Di „ „
$C_2HCl_3O_2$, Tri „ „
} Solids.

The acid contains a base C_2H_3O acetyl, which forms compounds, and the following relations therefore exist between acetic acid and alcohol.

Ethyl.	Acetyl.
CH_3	CH_3
CH_2	CO

So that aldehyde is $\left.\begin{matrix}CH_3\\CO\end{matrix}\right\}H$ Acetyl hydride,

and acetic acid $\left.\begin{matrix}CH_3\\CO\end{matrix}\right\}HO$ is acetyl hydrate.

ACETYL CHLORIDE, C_2H_3OCl. — Fuming colourless liquid.

Preparation.—

θ. (*a.*) $3HC_2H_3O_2 + PCl_3 = 3C_2H_3OCl + H_3PO_3$

(*b.*) $CH_4 + COCl_2 = C_2H_3OCl + HCl$

ACETYL ACETATE ($C_2H_3O_2C_2H_3O$).—(Acetic anhydride) oily liquid:

$$4NaC_2H_3O_2 + POCl_3 = 2C_2H_3O_2C_2H_3O + 3NaCl + NaPO_3$$

LACTIC, $HC_3H_5O_3$.—Two isomeric modifications—syrupy acid, liquid, with characteristic smell.

Occurrence.—Free in flesh (isomeric form).

Preparation.—By lactic fermentation. Milk, sugar, putrid cheese, and chalk are mixed together and allowed to ferment. The chalk is added to neutralise the acid and prevent coagulation of casein; a precipitate of calcic lactate is formed:

$$\underset{\text{Lactose.}}{C_6H_{12}O_6} = 2C_3H_6O_3$$

The precipitate is removed as fast as it is formed, otherwise it becomes soluble, and becomes converted into butyrate of lime:

$$2C_3H_6O_3 = \underset{\text{Butyric acid.}}{C_4H_8O_2} + 2CO_2 + 2H_2$$

The calcic lactate is decomposed by oxalic acid:

$$Ca2C_3H_5O_3 + H_2C_2O_4 = \sqrt{CaC_2O_4} = 2HC_3H_5O_3$$

Properties.—Syrupy acid liquid; heated to 130° C., it becomes a yellow solid, $C_6H_{10}O_5$ dilactic

acid; at 330° C. it loses water and is converted into lactide, $C_6H_8O_4$; lactide unites with ammonia to form lactamide, $C_3H_7NO_2$

By oxidizing agents, lactic acid is converted to formic acid:

$$C_3H_6O_3 + O_3 = 3HCHO_2$$

TABLE XXXI.

Action of heat on Ammonium Salts of foregoing Acids.

$NH_4C_2O_4 = 2H_2O + C_2O_2(2NH_2)$ (*Oxamide*).
$NH_4CHO_2 = H_2O + CHONH_2$ (*Formanide*).

(*If strongly heated.*)

$NH_4CHO_2 = 2H_2O + CHN$ (*Formonitril or Hydrocyanic Acid*).
$NH_4C_2H_3O_2 = H_2O + C_2H_3O_2NH_2$ (*Acetamide*).

Vegetable Acids.

Tartaric and Citric.

Tartaric, $H_2C_4H_4O_6$

This is the formula of four acids which are distinguished by physical properties, chemical tests, and action on polarised light. Only one is important, ordinary tartaric acid.

Occurrence. — Free and combined in vegetable life. Principal source *argol* or *tartar*, $KHC_4H_4O_6$, crude potassic bitartrate, which is precipitated during the fermentation of grape "must."

Preparation.—The argol is dissolved in boiling water, and neutralised with chalk.

$$\theta.\ 2KHC_4H_4O_6 + CaCO_3 = \underline{CaC_4H_4O_6} + K_2C_4H_4O_6 + CO_2 + H_2O$$

The precipitate is filtered off, and the filtrate mixed with calcic chloride:

$$K_2C_4H_4O_6 + CaCl_2 = \underline{CaC_4H_4O_6} + 2KCl$$

The two precipitates are next decomposed by dilute sulphuric acid:

$$2CaC_4H_4O_6 + 2H_2SO_4 = \underline{2CaSO_4} + 2H_2C_4H_4O_6$$

Properties.—Colourless crystals, soluble in water. The solution dissolves the hydrates of copper and iron, so that in presence of this acid the alkaline hydrates produce no precipitate with aqueous solution of the salts of these metals.

Reaction.—If heated with potassic hydrate it is decomposed.

$$\theta.\ H_2C_4H_4O_6 = H_2C_2H_3O_2 + H_2C_2O_4$$

All the tartrates are decomposed on ignition, leaving a carbonate.

Citric Acid, $H_3C_6H_5O_7$

Occurrence.—In juice of lemons and other fruit.

Preparation.—The juice is boiled with chalk.

$$\theta.\ 2H_3C_6H_5O_7 + 3CaCO_3 = \overline{Ca_3 2C_6H_5O_7 + 3CO_2 + 3H_2O}$$

The precipitate is decomposed by dilute sulphuric acid:

$$Ca_3 2C_6H_5O_7 + 3H_2SO_4 = \overline{3CaSO_4} + 2H_3C_6H_5O_7$$

Properties.—White crystals, soluble in water, acting towards the hydrates of Cu and Fe in a similar manner to tartaric acid.

TABLE XXXII.

Action of Heat on Citric Acid.

175° C.—$C_6H_8O_7 = \underset{\text{Aconitic acid.}}{C_6H_6O_6} + H_2O$

Above 175° C.—$C_6H_6O_6 = \underset{\text{Itaconic acid.}}{C_5H_6O_4} + CO_2$

$C_5H_6O_4 = \underset{\text{Citraconic acid.}}{C_5H_4O_3} + H_2O$

Fats and Oils—Saponification.

Oils are divided into two groups, fixed and volatile.

TABLE XXXIII.

Showing differences between Fixed and Volatile Oils.

Fixed.	*Volatile.*
Undergo saponification.	Will not saponify.
Lighter than water.	Generally heavier than water.
Composed of glyceryl and a fatty anhydride.	Composed of one or more hydrocarbons.
Leave a stain on paper.	Leave no stain on paper.
Cannot be distilled without decomposition.	Distil unchanged.

Fixed Oils.

Occurrence. — In vegetable and animal kingdoms. They are mostly transparent colourless liquids; the higher members of the group are crystalline solids.

One example will show the constitution of these bodies:

$HC_{16}H_{31}O_2$ = Palmitic acid.

$C_3H_5 3C_{16}H_{31}O_2$ = Palm oil, or palmitate of glyceryl.

$NaC_{16}H_{31}O_2$ = Hard soap, or palmitate of soda.

$C_3H_5 3HO$ = Glycerine, or glyceryl hydrate.

The fixed oils are subdivided into two groups—drying and non-drying.

The drying oils, if exposed to air, absorb oxygen, and increase in air and become hard.

The non-drying oils under similar conditions become rancid.

TABLE XXXIV.

Most important Fatty Acids and their Derivatives.

Acid.	Oil.	Soap.
$HC_{18}H_{33}O_2$ Oleic.	$(C_{18}H_{33}O_2)_3C_3H_5$ Olive.	$NaC_{18}H_{33}O_2$ Sodic oleate.
$HC_{16}H_{31}O_2$ Palmitic.	$(C_{16}H_{31}O_2)_3C_3H_5$ Palm.	$NaC_{16}H_{31}O_2$ Sodic palmitate.
$HC_{18}H_{35}O_2$ Stearic.	$(C_{18}H_{35}O_2)_3C_3H_5$ Stearine.	$NaC_{18}H_{35}O_2$ Sodic stearate.

SAPONIFICATION.

If a fixed oil be heated with a metallic oxide, in presence of water, the fatty acid unites with the new base, forming a salt; whilst the glyceryl unites with three molecules of HO to form glycerine:

$$C_3H_5\begin{cases}C_{16}H_{31}O_2\\C_{16}H_{31}O_2\\C_{16}H_{31}O_2\end{cases}+3NaHO=C_3H_5\begin{cases}HO\\HO\\HO\end{cases}+3NaC_{16}H_{31}O_2$$

Palm oil. Glycerine. Soda soap.

or

$$\underset{\text{Olive oil.}}{2(C_3H_5 3C_{18}H_{33}O_2)}+3PbO+3H_2O=2(C_3H_5 3HO)+\underset{\text{Lead soap.}}{3(Pb2C_{18}H_{33}O_2)}$$

The only soluble soaps are those of the alkalies.

If sodium is the base, a hard soap results; if potassium, then a soft soap.

If a strong acid be added to a soap the fatty acid is liberated:

$$NaC_{16}H_{31}O_2+HCl=NaCl+\underset{\text{Palmitic acid.}}{HC_{16}H_{31}O_2}$$

GLYCERINE, $C_3H_5 3HO$

Glycerine is a triatomic alcohol.

Properties.—A viscid liquid with a sweet taste, miscible in water in all proportions. It undergoes fermentation under favourable circumstances, producing propionic acid.

Preparation.—By distilling fixed oils with superheated steam, when they undergo decomposition into fatty acid and glycerine, both of which distil over.

Reactions.—If heated with a fatty acid under pressure an oil is formed.

θ. $C_3H_5 3HO + 3HC_{16}H_{31}O_2 = C_3H_5 3C_{16}H_{31}O_2 + 3H_2O$
Glycerine. Palmitic acid. Palm Oil.

If heated alone or with P_2O_5 acroleine is formed:

θ. $C_3H_8O_3 = C_3H_4O + 2H_2O$

Acroleine is a volatile liquid with peculiar odour.

TABLE XXXV.

Actions of Acids on Glycerine.

Dilute, HNO_3
$C_3H_5 3HO + O_2 = H_2O + C_3H_6O_4$, Glyceric acid.

Strong, HNO_3
$C_3H_5 3HO + 3HNO_3 = 3H_2O + C_3H_5(NO_2)_3O_3$ Nitro glycerine

Acetic Acid.

$C_3H_5 3HO + HC_2H_3O_2 = H_2O + C_3H_5 2HOC_2H_3O_2$
Mono-acetin.

$C_3H_5 3HO + 2HC_2H_3O_2 = 2H_2O + C_3H_5 HO2C_2H_3O_2$
Di-acetin.

$C_3H_5 3HO + 3HC_2H_3O_2 = 3H_2O + C_3H_5 3C_2H_3O_2$
Tri-acetin.

Hydrochloric Acid.

$C_3H_5 3HO + HCl = H_2O + C_3H_5 2HOCl$, Mono-chlorhydrin.
$C_3H_5 3HO + 2HCl = 2H_2O + C_3H_5 HOCl_2$, Di-chlorhydrin.

These are glyceric ethers, and are mostly oily liquids.

NITRO GLYCERINE.—Oily liquid; if subjected to cold becomes solid; explodes by percussion.

$$2C_3H_5 3NO_2 O_3 = 6CO_2 + 5H_2O + 3N_2 + O$$

It burns quietly if ignited. Dynamite is a porous earth impregnated with nitro glycerine.

CHLORHYDRINS.—Chlorine can only replace two molecules of hydroxyl directly through hydrochloric acid. To prepare trichlorhydrin the following method must be adopted:

θ. $C_3H_5HOCl_2 + PCl_5 = POCl_3 + HCl + C_3H_5Cl_3$

If dichlorhydrin be heated with KHO, it loses HCl and becomes C_3H_5ClO (*Epichlorhydrin*).

Cyanogen and its Compounds.

CYANOGEN, C_2N_2

Preparation.—θ. $Hg2CN = Hg + C_2N_2$

Properties.—Colourless gas with odour of bitter almonds. Inflammable, with a purplish flame, to CO_2 and N. It is soluble in water, but the solution is unstable.

$2CN + 4H_2O = (NH_4)_2C_2O_4$, oxalate ammonia.

It combines with potassium to form KCN, cyanide of potassium.

HYDROCYANIC ACID, HCN.

Preparation.—Occurs free in cassava juice, by passing H_2S over cyanide of mercury, and collecting product in a cooled receiver; this process gives the anhydrous acid. A dilute acid is prepared by distilling K_4FeCy_6 with dilute H_2SO_4. (See

Table, page 37.) The medicinal acid, prepared in this way, contains 2 per cent. of anhydrous acid.

Formed by fermentation, when bitter almonds are left in contact with water; the amygdalin takes up water:

$$C_{20}H_{27}NO_{11} + 2H_2O = \underset{\text{Oil of bitter Almonds.}}{C_7H_5HO} + \underset{\text{Glucose.}}{2C_6H_{12}O_6} + HCN$$

Reactions.—Decomposed slowly by water:

$$HCN + 2H_2O = NH_4CHO_2, \textit{ Ammonic formiate.}$$

If heated with KHO:

$$\theta.\ KHO + HCN + H_2O = KCHO_2 + NH_3$$

If the concentrated acid be mixed with HCl (aqueous):

$$HCN + 2H_2O + HCl = NH_4Cl + HCHO_2$$

It neutralises alkaline hydrates, forming cyanides.

CYANIDE OF POTASSIUM, KCy or KCN. — White crystalline solid.

Preparation.—

(*a.*) $\theta.\ 2KHO + C_3 + N_2 = 2KCN + CO + H_2O$

(*b.*) $\theta.\ K_4FeCy_6 = 4KCy + FeC_2 + N_2$

(*c.*) Usual process—

$$\theta.\ K_4FeCy_6 + K_2CO_3 = 5KCy + KCyO + Fe + CO_2$$

Reactions of Cyanides.—Great tendency to form double salts:

$$2NaCy + AgNO_3 = \underset{\text{Soluble.}}{(AgCyNaCy)} + NaNO_3$$

$$AgCyNaCy + AgNO_3 = \sqrt{2AgCy} + NaNO_3$$

If heated with water:

$$\theta.\ KCN + 2H_2O = KCHO_2 + NH_3$$

If heated in air:

$$\theta.\ KCN + O = KCNO,\ \textit{Cyanate of potash.}$$

$$\theta.\ 2KCNO + O_3 = K_2CO_3 + N_2 + CO_2$$

CYANIC ACID, HCNO.—Volatile liquid, with odour of SO_2

Preparation.—$\theta.\ H_3C_3N_3O_3 = 3HCNO$
Cyanuric acid.

Decomposed by water:

$$HCNO + 2H_2O = \sqrt{NH_4HCO_3},\ \textit{Cyamelide.}$$

The tendency of HCN to form double salts gives rise to the formation of ferro and ferrid cyanides.

The following table will show the constitution of these bodies.

TABLE XXXVI.

Ferrocyanide of Potassium,	$K_4FeCy_6 = 4KCy,FeCy_2$
Ferrid ,, ,,	$K_3FeCy_6 = 3KCyFeCy_3$

FERRO CYANIDE of POTASSIUM, K_4FeCy_6 (*Yellow Prussiate of Potash*).—Yellow crystals.

Preparation.—By fusing together scrap iron, carbonate of potass, and nitrogenous matter.

HYDROFERROCYANIC ACID, H_4FeCy_6.—Unstable liquid.

By precipitating K_4FeCy_6 in aqueous solution by tartaric acid.

FERRIDCYANIDE OF POTASSIUM, K_3FeCy_6 (*Red Prussiate of Potash*).—Red crystals.

Preparation.—

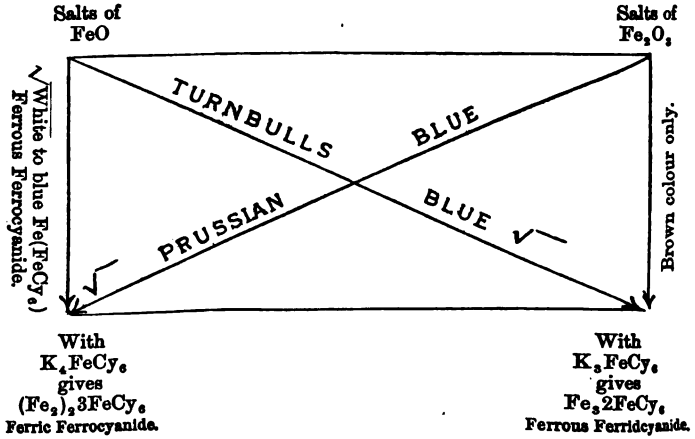
$$2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl$$

HYDROFERRIDCYANIC ACID, H_3FeCy_6

$$Pb_3 2FeCy_6 + 3H_2S = \sqrt{3PbS} + 2H_3FeCy_6$$

Colourless liquid, very unstable.

Diagram showing function of these Salts in testing for Iron.


Salts of FeO
Salts of Fe_2O_3
TURNBULLS BLUE
PRUSSIAN BLUE
White to blue Fe(FeCy6) Ferrous Ferrocyanide.
Brown colour only.
With K_4FeCy_6 gives $(Fe_2)_2 3FeCy_6$ Ferric Ferrocyanide.
With K_3FeCy_6 gives $Fe_3 2FeCy_6$ Ferrous Ferridcyanide.

Action of KHO *on these Salts.*

$$(Fe_2)_2 3FeCy_6 + 12KHO = \sqrt{2Fe_2O_3} + 3K_4FeCy_6 + 6H_2O$$

$$Fe_3 2FeCy_6 + 8KHO = \sqrt{Fe_2}6HO + \sqrt{Fe}2HO + 2K_4FeCy_6$$

SULPHOCYANIC ACID, HCNS.

Preparation of potassium sulphocyanide:

$$\theta.\ \begin{cases} K_4FeCy_6 + 3S_2 = 4KCNS + Fe2CNS \\ Fe2CNS + K_2CO_3 = 2KCNS + FeCO_3 \end{cases}$$

TABLE XXXVII.

Principal Reactions of Ferrocyanide of Potassium.

$\theta.\ K_4FeCy_6 = 4KCy + FeC_2 + N_2$

$\theta.\ K_4FeCy_6 + K_2CO_3 = 5KCy + KCyO + Fe + CO_2$

$\theta.\ K_4FeCy_6 + 3S_2 = 4KCNS + Fe2CNS$

$K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl$

$K_4FeCy_6 + 2Fe_2Cl_6 = \sqrt{Fe_7Cy_{18}} + 12KCl$ (Prussian blue.)

$K_4FeCy_6 + FeSO_4 = K_2SO_4 + \sqrt{K_2Fe_2Cy_6}$

UREA, $CO2NH_2$.—*Carbamide*, white crystalline solid.

Occurrence.—In urine of mammalia.

Preparation.—(*a.*) Synthetical production:

$\theta.\ 2KHO + C_3 + N_2 = 2KCN + CO + H_2O$

$\theta.\ KCN + PbO = KCNO + Pb.$

$2KCNO + (NH_4)_2SO_4 = 2NH_4CNO + K_2SO_4$ (Ammonium cyanate.)

$\theta.\ NH_4CNO = CO2NH_2$

If sulphocyanate of ammonia be substituted for cyanate, sulphur urea is formed, $CS2NH_2$

$$\theta.\ NH_4CNS = CS2NH_2$$

(*b.*) From urine:

Concentrate urine and filter; add oxalic acid:

$$CO2NH_2 + H_2C_2O_4 = \underbrace{2CO2NH_2.H_2C_2O_4}_{\text{Oxalate of urea.}}$$

$$\underbrace{2CO2NH_2H_2C_2O_4}_{\text{Filter and crystallise.}} + CaCO_3 = CaC_2O_4 + CO_2 + H_2O + 2CO2NH_2$$

(*c.*) $COCl_2 + 2NH_3 = 2HCl + CO2NH_2$

(*d.*) $\theta.\ \underbrace{NH_4NH_2CO_2}_{\text{Amm. carbamate.}} = H_2O + CO2NH_2$

This last reaction proves urea to be an amide carbonic acid.

Reactions.—Decomposed by nitrous acid:

$$CO2NH_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O$$

Also by chlorine:

$$\theta.\ 6(CO2NH_2) + 3Cl_2 = \underbrace{2C_3H_3N_3O_3}_{\text{Cyanuric acid.}} + 4NH_4Cl + 2HCl + N_2$$

In presence of a ferment it is decomposed:

$$CO2NH_2 + 2H_2O = (NH_4)_2CO_3$$

It forms sparingly soluble salts with nitric and oxalic acids.

Nitrate—$CO2NH_2HNO_3$

Oxalate—$2(CO2NH_2)H_2C_2O_4$

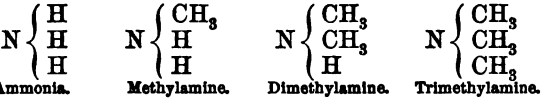
Being a weak base, it does not form salts with weak acids; hence—

$$2(CO2NH_2.HNO_3) + BaCO_3 = 2(CO2NH_2) + Ba2NO_3 + CO_2 + H_2O$$

Amines.

Definition.—A compound radical derived from a single molecule of ammonia (NH_3), in which the hydrogen is wholly or partially displaced by an alcoholic radical.

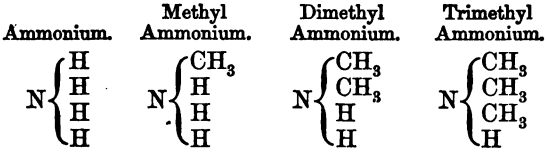
Examples.

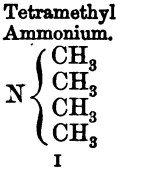


Ammonia. Methylamine. Dimethylamine. Trimethylamine.

If derived from a molecule of ammonium, NH_4, then it forms an alcoholic ammonium.

Examples.





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The amines are formed by heating the iodides or bromides of alcoholic radicals with alcoholic ammonia in sealed tubes:

$$\underset{}{NH_3} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Ethyl ammonium iodide.}}{NH_2CH_3HI}$$

$$NH_3 + 2CH_3I = NH(CH_3)_2HI + HI$$
$$NH_3 + 3CH_3I = N(CH_3)_3HI + 2HI$$

And then distilling with potassic hydrate:

$$NH_2CH_3HI + KHO = KI + H_2O + \underset{\text{Methylamine.}}{NH_2CH_3}$$

All the amines have a strong resemblance to ammonia. The lower members are gases with an ammoniacal odour, and soluble in water. They act as bases and are combustible.

METHYLAMINE, CH_3NH_2

Preparation.—As above;

also

$$\theta.\ \underset{\text{Methyl cyanate.}}{CH_3CNO} + 2KHO = K_2CO_3 + NH_2CH_3$$

Properties.—Colourless gas, with ammoniacal odour. Soluble in water; forming a solution analogous to NH_4HO. Like its analogue it is alkaline; is neutralised with acids to form salts.

$$NH_2CH_3 + HCl = \underset{\text{Methylamine hydrochloride.}}{NH_2CH_3HCl}$$

It precipitates hydrated oxides from solution of metallic salts, and the hydrochloride is decomposed if heated with calcic oxide.

$$\theta.\ 2(NH_2CH_3HCl) + CaO = CaCl_2 + H_2O + NH_2CH_3$$

DIMETHYLAMINE, NH2CH$_3$.—A gas.

TRIMETHYLAMINE, N3CH$_3$.—A gas, exists in herring brine.

TETRAMETHYL AMMONIUM.

Preparation.—If iodide of methyl is added to trimethylamine N(CH$_3$)$_3$, they unite with explosion.

$$CH_3I + N3CH_3 = N4CH_3.I$$

Tetramethyl ammonium iodide.

A white crystalline salt, soluble in water. If this solution be heated with oxide of silver—

$$\theta.\ 2(N4CH_3.I) + Ag_2O + H_2O = \sqrt{2AgI} + 2(N4CH_3.HO)$$

This latter body is the hydrate of tetramethyl ammonium. It is decomposed on heating.

$$\theta.\ N4CH_3.HO = CH_3HO + N3CH_3$$

Methyl alcohol. Trimethylamine.

Aromatic Compounds.

BENZOL, PHENOL, BENZOIC ACID, OIL OF BITTER ALMONDS.

The relations between these substances will be seen by the following table :—

TABLE XXXVIII.

Showing Relations of Aromatic Group.

METHYL HYDRIDE.	BENZOL.
CH_3H	C_6H_5H
METHYL ALCOHOL.	PHENOL.
CH_3HO	C_6H_5HO
Replacing an atom of *H in CH_3 by CH_3 we get ethyl alcohol.	Replacing an atom of H in CH_3 by C_6H_5 we get benzyl alcohol.
CH_2CH_3HO	$CH_2C_6H_5HO$
Abstract two atoms of H we get aldehyde.	Abstract two atoms of H we get benzyl aldehyde or oil of bitter almonds.
$CHCH_3O$	†CHC_6H_5O
Add an atom of O we get acetic acid.	Add an atom of O we get benzoic acid.
$CHCH_3O_2$	$CHC_6H_5O_2$

BENZOL, C_6H_6.

Occurrence.—Exists in coal tar.

Preparation.—(*a.*) By fractionally distilling coal tar.

(*b.*) By heating benzoic acid with lime.

$$\theta.\ C_7H_6O_2 + CaO = CaCO_3 + C_6H_6$$

* See page 106.

† The radical C_7H_5O is sometimes called benzoyl.

Properties.—Colourless refractive liquid, with characteristic smell. Insoluble in water. Solvent for I, S, P, and fats.

Unites with H_2SO_4 to form sulpho-phenylic acid—

$$C_6H_5HSO_3$$

Both chlorine and bromine displace hydrogen atoms, forming

C_6H_5Cl, Chloro benzol.
C_6H_5Br, Bromo benzol.

Nitric acids converts it into nitro benzol:

$$C_6H_6 + HNO_3 = H_2O + C_6H_5NO_2$$

This latter, under the action of reducing agents such as H_2S or H, becomes converted into aniline:

$$C_6H_5NO_2 + 3H_2 = 2H_2O + C_6H_5NH_2$$

PHENOL, or CARBOLIC ACID, C_6H_5HO

Occurrence.—In coal tar.

Properties.—Tar is fractionally distilled; a portion of the heavy distillate is agitated with sodic hydrate. This dissolves the carbolic acid, which is precipitated by hydrochloric acid.

It can be prepared by direct oxidation of benzol in presence of Al_2Cl_6

Properties.—Colourless crystalline solid, with characteristic odour; neutral to test paper, yet acting as an acid towards metallic oxides. It is a powerful corrosive and antiseptic.

Reactions.—The carbolates or phenates are decomposed by CO_2 in presence of alkaline hydrates, forming salicylates.

$$C_6H_5HO + CO_2 = \underset{\text{Salicylic acid.}}{HC_7H_5O_3}$$

If heated with nitric acid it is converted into picric acid, a yellow crystalline body.

$$\theta.\ C_6H_5HO + 3HNO_3 = 3H_2O + C_6H_23NO_2.HO$$

BENZOIC ACID, $C_7H_6O_2$

Occurrence.—In gum benzoin.

Preparation.—By sublimation from the gum.

Properties.—White feathery crystals, with aromatic odour; soluble in water.

Reaction.—Decomposed by heat.

$$\theta.\ C_7H_6O_2 = C_6H_6 + CO_2$$

BENZYL ALDEHYDE, C_7H_6O

Occurrence.—Essential oil of bitter almonds.

Properties.—Colourless refractive liquid, with aromatic taste and odour.

Reaction.—It absorbs oxygen readily, being converted into benzoic acid.

By the action of nascent hydrogen it is converted into benzyl alcohol.

$$C_7H_6O + H_2 = C_7H_7HO$$

It is decomposed by heat.

$$\theta.\ C_7H_6O = CO + C_6H_6$$

Chlorine converts it into benzoyl chloride.

$$C_7H_6O + Cl_2 = HCl + C_7H_5OCl$$

BENZYL ALCOHOL, C_7H_7HO

Properties.—Colourless oily liquid, with aromatic odour.

Preparation.—By heating oil of bitter almonds with potassic hydrate.

$$2C_7H_6O + KHO = \underset{\text{Potassic benzoate.}}{KC_7H_5O_2} + \underset{\text{Benzyl alcohol.}}{C_7H_7HO}$$

Reaction.—If heated with nitric acid it takes up oxygen:

$C_7H_8O + O = H_2O + C_7H_6O$ (*Oil of bitter almonds*).

If heated with chromic acid it takes up another atom of oxygen:

$C_7H_8O + O_2 = H_2O + C_7H_6O_2$ (*Benzoic acid*).

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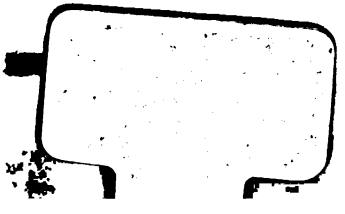
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